WL-TR-96-3145

ADVANCED STREAMING AGENT DEVELOPMENT

VOLUME II: METAL COMPOUNDS

PATTERSON, R.A., GOBELI, G.W.,
BRABSON, D. AND TAPSOTT, R.E.

NEW MEXICO ENGINEERING RESEARCH INSTIT.
THE UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NM 87131-1376

APRIL 1996

INTERIM REPORT FOR 08/01/95-03/01/96

19970224 112
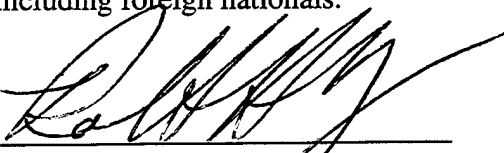
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ROBERT A. TETLA
Project Officer

ALLEN D. NEASE
Chief, Infrastructure Technology Section

RICHARD N. VICKERS
Chief, Air Base Technology Branch

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE APR 1996	3. REPORT TYPE AND DATES COVERED INTERIM 08/01/95--03/01/96

4. TITLE AND SUBTITLE ADVANCED STREAMING AGENT DEVELOPMENT
VOLUME II: METAL COMPOUNDS

6. AUTHOR(S) PATTERSON, R.A., GOBELI, G.W., BRABSON, D. AND TAPSOTT, R.E.

5. FUNDING NUMBERS
C S-5000.31
PE 61101
PR 2673
TA 30
WU 03

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

New Mexico Engineering Research Institute
The University of New Mexico
Albuquerque, New Mexico 87131-1376

8. PERFORMING ORGANIZATION REPORT NUMBER

NMERI 96/3/32540

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
FLIGHT DYNAMICS DIRECTORATE
WRIGHT LABORATORY
AIR FORCE MATERIEL COMMAND
Tyndall Air Force Base, Florida 32403-5323
POC: MAJOR ROBERT TETLA, WL/FIVCF, DSN 523-3734

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

WL-TR-96-3145

11. SUPPLEMENTARY NOTES REPORT GENERATED FOR WL/FIVCF AND APPLIED RESEARCH ASSOCIATES, INC

12a. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The objective of the overall effort is to develop new chemical compounds as Halon 1211 replacements. Four families of compounds are particularly promising—phosphorus nitrides, metal compounds, silicon compounds, and tropodegradable halocarbons. This report is Volume II of a 5-volume series of reports. Volume I covers silicon compounds; Volume III, phosphorus compounds, Volume IV, tropodegradable halocarbons; and Volume V, laboratory-scale streaming tests. The portion of the work presented in this document reviews metal compounds as candidates as Halon 1211 substitutes and reports laboratory-scale testing of these compounds.

14. SUBJECT TERMS
Halon 1211; Halon replacement; Metal; Complex; Organometallic Advanced agent; Streaming agent

15. NUMBER OF PAGES
106

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

CONTENTS

CONTENTS
(CONTINUED)

CONTENTS
(CONCLUDED)

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AAWG	Advanced Agent Working Group
AFOSR	Air Force Office of Scientific Research
ARA	Applied Research Associates
CGET	Center for Global Environmental Technologies
CCD	charged-couple-device
CNS	central nervous system
FC	perfluorocarbon
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HRBB	heat removed by the burner
IR	infra-red
LC_{50}	concentration required to cause death in 50 percent of an animal test population
LC_{LO}	lowest concentration causing death
LD_{50}	dose required to cause death in 50 percent of an animal test population
LD_{LO}	lowest dose causing death
LSDE	Laboratory-Scale Discharge Extinguishment
NIST	National Institute of Standards and Technology
NMERI	New Mexico Engineering Research Institute
PFC	perfluorocarbon
TC_{LO}	lowest concentration having a toxic effect
USAF	U.S. Air Force
WL/FIVCF	Wright Laboratories

LIST OF UNITS

h	hour
kg	kilogram
mg	milligram
m	meter
min	minute
ppm	parts per million

PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico, for the Infrastructure Technology Section of Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates (ARA), Inc., Tyndall Air Force Base, Florida, under SETA Task 3.12, Air Force Contract S-5000.31, NMERI Number 8-32540. This document is Volume II of the final report and provides an assessment of metal compounds as potential substitutes for replacement of Halon 1211 in streaming applications.

The Start Date for the overall Advanced Streaming Agent Program was 9 August 1995, and the End Date was April 30 1996. The WL/FIVCF Project Officer is Major Robert A. Tetla, the ARA Project Officer is Michael A. Rochefort, and the NMERI Principal Investigator is Robert E. Tapscott.

NMERI 96/3/32540

EXECUTIVE SUMMARY

A.   OBJECTIVE

The objective of the overall effort is to develop new chemical compounds that are highly efficient fire suppressants, are environmentally and toxicologically benign, have the same performance characteristics as Halon 1211, and are compatible with existing fire extinguishing equipment and aircraft materials. The effort includes (1) synthesis of the new compounds; (2) laboratory analysis of fire suppression characteristics; (3) analysis of environmental and toxicity parameters; and (4) analysis of stability, compatibility, and manufacturability factors. The outcome of the effort is the identification of the most promising replacement candidates for follow-on medium- and large-scale testing.

This document is Volume II of the final report and provides an assessment, including laboratory-scale testing, of metal compounds as potential substitutes for replacement of Halon 1211 in streaming applications. The five volumes of the final report are listed below:

Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development, Volume I: Silicon Compounds*, WL-TR-96-XX, Vol. 1 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/1/32540

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Heinonen, E. W., Lifke, J. L., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume IV: Tropodegradable Halocarbons*, WL-TR-96-XX, Vol. 4 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/4/32540

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B.   BACKGROUND

Under the Montreal Protocol, an international treaty enacted in 1987 and amended in 1990, 1992, and 1995, the production of the fire and explosion protection agents Halon 1211 (bromochlorodifluoromethane, BCFC-12B1, $CBrClF_2$) and Halon 1301 (bromotrifluoromethane, BFC-13B1, CF_3Br) was phased out in the United States at the end of 1993.[*] To date, no environmentally acceptable halon substitute, equivalent to the existing halons in toxicity, effectiveness, and dimensionality, has been identified.

Halocarbons as replacements for halons have been well studied, and it is unlikely that new, exceptionally effective, halon replacements will be identified among the standard, saturated, non-iodinated halocarbons. The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios and usually exhibit higher toxic gas emissions during fire suppression. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs. The single partial success among halocarbon replacements are the iodides, in particular, trifluoromethyl iodide (CF_3I) which is as effective as the existing halons. However, the cardiosensitization by the fluoroalkyl iodides that have been investigated restricts their use to only certain applications. There is, therefore, an increasing incentive to look at compounds other than the usual, saturated halocarbons. These compounds are the non-halocarbon candidates, known as "advanced agents." The most promising of these are the phosphorus compounds (particularly, the phosphorus nitrides, which include phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon compounds. In addition, the special class of tropodegradable halocarbons are promising candidates.

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[*]See Volume IV of this series of reports for an overview of halocarbon numbers (e.g., "BCFC-12B1" and "BFC-13B1") and general information on halocarbon nomenclature.

C.   SCOPE

An investigation of advanced fire suppression agents is being conducted to find a replacement for Halon 1211 used in Air Force flightline and aircraft portable fire extinguishers. Four separate tasks are included in the overall effort:

Task 1: Technical Review. A technical review of syntheses, characterization, properties, toxicity, and fire extinguishment data (if any) for phosphorus nitrides, metal complexes, and silicon compounds that may have utility as fire and explosion protection agents is to be conducted.

Task 2: Synthesis of New Compounds. Samples of the most promising of these materials based on expected toxicity, availability/manufacturability, and environmental characteristics are to be prepared or obtained.

Task 3: Laboratory Evaluations. Laboratory-scale evaluations of fire extinguishment by these materials are to be performed. Preliminary analyses of global environmental impact, toxicity evaluations, and manufacturing/synthesis assessment of the candidates identified for follow-on testing are to be conducted.

Task 4: Final Report. The information obtained is to be used to prepare a final report detailing the work performed, the results obtained, and conclusions. The report will make recommendations for continuation of large-scale testing with the most promising agents.

D.   METHODOLOGY

The rationale for using metal compounds for replacements for halons is based on the superior fire suppression capabilities of some iron compounds and the fact that metal compounds are expected to have zero ozone depletion potentials (ODP), global warming potential (GWP), and atmospheric lifetimes. A historical review of the use of metal compounds as fire suppression agents was coupled with a description of work performed to determine suppression mechanisms of iron compounds to form the basis for determining which compounds would potentially be the most efficient halon replacements.

E.   APPROACH

The processes by which metal compounds extinguish fires are considered critical in determining the most effective compounds for replacing halons. A historical review of past research into metal compounds, including dry chemicals, was performed. Since iron compounds have been demonstrated to have fire extinguishing efficiencies 10 times that of Halon 1301, they will form the initial core of the investigation. Extinguishment mechanisms of iron pentacarbonyl ($Fe(CO)_5$) have been investigated in depth at The University of New Mexico (UNM) and the National Institute of Standards and Technology (NIST). While iron pentacarbonyl is too toxic to be considered as a fire extinguishing agent, the mechanisms are applicable to other iron compounds and metal compounds in general. A review of this work is also presented. A description of other iron compounds, including synthesis and test results, is included. Finally, a review of the toxicity of metal compounds has been conducted and results presented. Recommendations regarding future work are listed.

F.   RESULTS

Iron pentacarbonyl ($Fe(CO)_5$) was tested under various conditions in the UNM Sapphire burner to determine its effects on pre-mixed methane flames. It was proven that the iron-containing extinguishants catalytically inhibit the flame. Based on the historical review, three compounds, tris(acetylacetonato)iron(III) – ($Fe(acac)_3$, tris(trifluoroacetylacetonato)iron(III) - $Fe(tfac)_3$, and tris(hexafluoroacetylacetonato) iron(III) - $Fe(hfac)_3$, were synthesized and tested in the UNM Sapphire burner and the Laboratory-Scale Discharge Extinguishment (LSDE) apparatus. While the $Fe(acac)_3$ and $Fe(hfac)_3$ exhibited good fire suppression capability in the Sapphire apparatus, they were found to be nearly insoluble in the initially tested solvents and showed no improvement over pure solvent performance in the LSDE experiments. This is potentially because the iron compounds were introduced as vapors or aerosols in the Sapphire testing, while they were dilute liquid mixtures in the LSDE testing. A review of toxicity has indicated that while metals themselves may not be toxic, compounds vary in the hazard presented to humans. Ligands, especially, vary in toxicity and physical properties from complexes.

G.   CONCLUSIONS

Metal-containing compounds are very effective fire extinguishing agents, and some are known to be more effective than Halon 1301 (CF_3Br) due primarily to catalytic recombination of flame radicals. There is not a complete understanding of the details of extinguishment by iron containing compounds, which are perhaps the most thoroughly studied of the metal containing compounds outside of the Group IA and Group IIA metals. Several metals, in addition to iron, and including manganese, offer significant promise. The importance of delivery techniques (such as misting, dry aerosol generation, etc.) is recognized, but there is far too little information on the influence of the technique on the effectiveness of the agent. Finally, there are insufficient data on toxicity to be able to make generalizations on which compounds would exhibit acceptable toxicity; each metal compound must be investigated individually.

H.   RECOMMENDATIONS

It is recommended that metal compounds be retained in the competition for next generation agent(s), and that using iron compounds as a baseline, work continue to elucidate the details of the extinguishing mechanism(s). Manganese should be selected as a second metal for study, and that the results from examination of this metal should be compared and contrasted with the data for the iron compounds. Using iron compounds as a baseline, the effects of potential delivery techniques should be examined in premixed flames, counter-flow diffusion flames, and misting systems. As a minimum, the following techniques should be investigated: dry powder, aqueous aerosols (both with and without evaporation of the water), and non-aqueous mists. Finally, the toxicity of those compounds selected for further study should be researched concurrently with extinguishement testing.

SECTION I

INTRODUCTION

A.   OBJECTIVE

The objective of the overall effort is to develop new chemical compounds that are highly efficient fire suppressants, are environmentally and toxicologically benign, have the same performance characteristics as Halon 1211, and are compatible with existing fire extinguishing equipment and aircraft materials. The effort includes (1) synthesis of the new compounds; (2) laboratory analysis of fire suppression characteristics; (3) analysis of environmental and toxicity parameters; and (4) analysis of stability, compatibility, and manufacturability factors. The outcome of the effort is the identification of the most promising replacement candidates for follow-on medium- and large-scale testing.

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B. BACKGROUND

Under the Montreal Protocol, an international treaty enacted in 1987 and amended in 1990, 1992, and 1995, the production of the fire and explosion protection agents Halon 1211 and Halon 1301 was phased out in the United States at the end of 1993. To date, no environmentally acceptable halon substitute that is equivalent to the existing halons in toxicity, effectiveness, and dimensionality has been identified.

Halocarbons as replacements for halons have been well studied, and it is unlikely that new, highly effective, halon replacements will be identified among the typical non-iodinated haloalkanes. The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs (for an overview, see Reference 1). The single partial success among halocarbon replacements are the iodides, in particular, trifluoromethyl iodide (CF_3I), which is as effective as the existing halons. However, the toxicity of the iodides restricts their use to only certain applications. There is, therefore, an increasing incentive to look at compounds other than the typical haloalkanes. These compounds are the non-halocarbon candidates, known as "advanced agents" and a special class of halocarbons, the "tropodegradable" halocarbons.

Recent work has identified several potential non-halocarbon (References 2 and 3) and low-atmospheric-lifetime halocarbon (Reference 4) substitutes for halon fire extinguishants. In particular, work by the Advanced Agent Working Group, AAWG, which includes U.S. Air Force (USAF) and U.S. Army participation, has shown that the most promising of the non-halocarbon compounds are phosphorus compounds (particularly, phosphorus nitrides, which include the phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon compounds

(Reference 5). The AAWG work (which emphasizes chemical options for total-flood Halon 1301 applications) and work by the USAF also show that tropodegradable halocarbons, which contain features that induce short atmospheric lifetimes, exhibit high promise.

C.   SCOPE

Four separate tasks are included in the overall effort:

Task 1: Technical Review. A technical review of syntheses, characterization, properties, toxicity, and fire extinguishment data (if any) for phosphorus nitrides, metal complexes, and silicon compounds that may have utility as fire and explosion protection agents is to be conducted.

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D.   APPROACH

The processes by which metal compounds extinguish fires are considered critical in determining the most effective compounds for replacing halons. A historical review of past research into metal compounds, including dry chemicals, was performed. Since iron compounds have been demonstrated to have fire extinguishing efficiencies 10 times that of Halon 1301, they will form the initial core of the investigation. Extinguishment mechanisms of iron pentacarbonyl

(Fe(CO)₅) have been investigated in depth at The University of New Mexico (UNM) and the National Institute of Standards and Technology (NIST). While iron pentacarbonyl is too toxic to be considered as a fire extinguishing agent, the mechanisms are applicable to other iron compounds and metal compounds in general. A review of this work is also presented. A description of other iron compounds, including synthesis and test results, is included. Finally, a review of the toxicity of metal compounds has been conducted and results presented. Recommendations regarding future work are listed.

SECTION II
BACKGROUND

A. INTRODUCTION

The use of metal-containing compounds as fire extinguishing agents has a long and distinguished tradition. McCamy, Shoub, and Lee commented that this tradition dates to the early part of this century and may extend into the last century, and noted that D. J. Block applied for a patent on a sodium bicarbonate dry chemical fire extinguisher in 1928 (Reference 6). The motivation for selecting sodium bicarbonate doubtless stemmed from the notion that, since thermal decomposition of the sodium bicarbonate yields CO_2, one should be able to use sodium bicarbonate as a novel agent for delivering CO_2 to a fire. However, when one compares the amount of CO_2 actually delivered by a dry chemical extinguisher with its superior performance vis-a-vis a conventional CO_2 extinguisher, it is apparent that the effectiveness of the dry chemical agents can not be accounted for by this appealing but inadequate notion. It was suspected early that the metal (sodium) was playing a key role; moreover, it was not obvious that the anion was completely unimportant. As a result, an especially rich literature has developed over the last 35 years, and contributions continue to this day. This literature has extended the exploration to a study of numerous metals, and the role of a variety of anions has also been investigated. In a survey of this literature, nearly 140 different compounds, with 33 different metals, have been cataloged. These data are summarized in Appendix A.

The objective of this section is to review a large fraction of the available literature, lay out the areas of agreement and disagreement, and provide some insights into the work yet needed. At the conclusion of this review, the reader will be aware of the extraordinary complexity of the subject. A single example from the early work of McCamy, Shoub, and Lee dramatically illustrates some of the tremendous complexities; these workers found that a commercial dry chemical formulation of $NaHCO_3$ ranked among the best of the compositions tested, while undried $NaHCO_3$ was dead last in the list (below portland cement, talc, and fire clay) (Reference 6).

5

In addition to the material presented here, the reader may also wish to consult some of the other excellent reviews of this literature. Fristrom surveyed the literature through 1966, and commented on the state of combustion suppression work to that date (Reference 7). In his comprehensive review of high temperature vapors, written about a decade later, Hastie included a large block on fire suppression and specifically addressed many of the factors involved in fire suppression by metal-containing compounds (Reference 8). Most recently, NIST prepared a broad survey of fire suppression literature as a baseline for proposing candidates for next generation fire suppression agents (Reference 9).

B.   MEASUREMENTS OF EFFECTIVENESS

There are almost as many techniques for measuring effectiveness as there are workers in the field. The techniques range at one extreme from those that are designed to test the effectiveness of the agent against a particular type of fire, to those at the other extreme that are designed to explore the basic chemistry of the extinguishment mechanisms. From the vantage point of transition of the technology to practice, the test of a particular agent against a particular fire is the most important. However, such an experiment provides very little information as to the basic reasons why an agent does or does not work. Moreover, if one examines the effectiveness of an agent against a particular type of fire, it may not be evident that an "ineffective" agent may be quite effective against a fire of another sort. Thus there is a need for examination of the basic science of the interactions at the molecular level, especially to provide insights that will assist in the development of new materials and techniques. Needless to say, basic science too has its limitations. The detailed chemistry of a molecule is important only if the molecule is present in sufficient concentrations at the critical point in the flame. For this reason, the various experiments that have been performed have complemented one another, and researchers have been well served to date by the wide diversity of experiments that have been performed with an eye toward determining the extinguishing effectiveness of potential agents with widely differing properties.

1.   Direct Observation of Extinguishment

The most direct measurement of the effectiveness of an agent is simply this: It extinguished the fire. Of course, much more can be learned from these experiments; one can evaluate the minimum amount of agent needed to extinguish the fire reliably, and can make qualitative observations that are indicative of important underlying mechanisms.

The experiments of McCamy, Shoub, and Lee, are elegant in their simplicity (Reference 6). In this work, various powders were used in a commercial "stored pressure" device to extinguish a leaded-gasoline fire on a 4-ft^2 concrete pad, and the measure of effectiveness was the qualitative assessment of two qualified observers. One of the significant results of this work was the dramatic demonstration of the importance of the physical properties (particle size, tendency to pack, etc.) of the powders.

Altman et al. examined a variety of existing and candidate dry chemical agents in a situation simulating a fuel leak onto a hot engine in an aircraft engine nacelle (Reference 10). Since a principal criterion was delayed re-ignition, relatively volatile agents such as CI_4 and $NH_4H_2PO_4$ vaporized (i.e., did not remain as powders) and scored poorly in this study; it is immediately recognized that these two materials are excellent agents in other scenarios.

Ewing et al. have studied the comparative effects of very finely divided powders using small heptane pan fires; in these experiments, the authors paid particular attention to the "limiting" particle diameter, which may be defined as follows (Reference 11). If the particle is smaller than the "limiting" diameter, it absorbs the maximum amount of heat of which it is capable by an increase in its translational energy, volatilization, and perhaps decomposition. Typical "limiting" diameters are 14 microns for K_2CO_3 and 35 microns for $K_2C_2O_4 \cdot H_2O$. Contrary to expectation, $K_4Fe(CN)_6 \cdot 3H_2O$, was significantly more effective than predicted based solely on thermal mechanisms.

2.   Direct Observation of Inerting

In closely related experiments, combustible mixtures of fuel and oxidizer were premixed with varying amounts of the extinguishing material, and the amount of extinguishing agent that prevented propagation of a flame in the mixture was sought. A variety of different

initiation schemes were employed. In experiments by Morrison and Scheller, a hot wire was used as the ignition source for mixtures of extinguishing agent, air, and methane or propane (Reference 12). It is of particular interest that the results of these experiments do not correlate particularly well with results of other techniques; these results may be "trying to tell us something" about the details of the inhibition and inerting mechanisms.

3.   Temperature Rise as a Measure of Inhibition

On a cooled, flat-flame burner, inhibition results in a rise in the temperature of the gases above the burner. Because quenching reduces heat absorbed by the burner, and some lift-off occurs, the temperature of the gases rises to a higher value. In the case of $NaHCO_3$, Iya et al. demonstrated that there was an essentially linear relationship between ΔT and $[Na]$, and concluded that this was conclusive proof of a homogeneous extinguishment mechanism (Reference 13).

4.   Propagation Velocity as a Measure of Inhibition

Several laboratories have made direct measurements of the speed of propagation of a flame front through a combustible mixture, and used the change in speed as a measurement of the degree of inhibition; other groups have used a related property such as the shape of the flame to deduce the flame speed.

To study the potential of suppression agents for sheathed explosives (for mining applications), Dolan and Dempster premixed powders with methane and air in a propagation tube (Reference 14). The rate of propagation of the flame was then studied as a function of the concentration of the powder. It was estimated that the minimum temperature necessary to propagate a flame in a methane-air mixture is 1330 °C (1600 K). It was found that, for the most part, the salts that performed best were those that decomposed below 200 °C (392 °F) and for which the surface area was a dominant factor. There were some surprises with respect to "conventional wisdom." For example, the order of effectiveness of the potassium halides was KF > KI > KCl; however, in most other studies, KF has been shown to be the least effective of these salts, and sometimes is completely ineffective.

For Bunsen-type flames, the area of the inner boundary of the luminous cone is directly related to flame speed, and can be estimated by several different techniques. Often, it is adequate to image the flame on a suitable screen or photographic plate and estimate the area from the two-dimensional image; schlieren techniques (which also generate two-dimensional images) take advantage of the large temperature increase at the inner boundary of the luminous cone. (For a variation on the schlieren technique, see the work of Gilbert [Reference 15]). Lask and Wagner used measurements of the area of the inner boundary to investigate the extinguishing efficiencies of several volatile metal compounds; the criterion used by these authors was a 30 percent reduction in flame speed (Reference 16). Among the materials studied was $Fe(CO)_5$. It is important to note that, while flame speed drops very sharply for small additions of $Fe(CO)_5$, further additions (not studied by these authors) have much less dramatic effects.

5.   Heat Extracted by the Burner as a Measurement of Inhibition

It has been shown by Botha and Spalding that the heat extracted from the flame by a cooled burner bears a very nearly linear relationship to flame speed (Reference 17). Brabson et al. have used the heat extraction technique to study some of the details of the inhibition of atmospheric methane-air flames by $Fe(CO)_5$, and found that this compound had a much larger effect when added to fuel-rich flames than when added to fuel-lean flames. Although there was a net inhibition of all flames, regardless of the fuel-oxidizer equivalence ratio, the significantly smaller effectiveness for fuel-lean flames suggests that the $Fe(CO)_5$ was promoting some aspect of the combustion in those flames (Reference 18).

6.   Measurement of Strain Rate in Counterflow Diffusion Flames

In counterflow diffusion flames, the flame front takes up a position relative to the stagnation plane that depends on the flame speed. A measurement of the location of the flame front then yields the strain rate, which is a measurement of inhibition. By varying the diluent fractions in the oxidizer and fuel steams, Linteris and Reinelt were able to establish the flame front either on the fuel side of the stagnation plane or on the oxidizer side of this plane, and discovered that the effect of $Fe(CO)_5$ on a flame is dependent on the stoichiometry of the flame and on the location of the flame front with respect to the stagnation plane (References 19 and

20). With the flame on the fuel side of the stagnation plane, the $Fe(CO)_5$ has a negligible effect when added to either stream. When the flame is on the oxidizer side, addition of $Fe(CO)_5$ to the fuel stream results in an apparent promotion of combustion, while addition of $Fe(CO)_5$ to the oxidizer stream results in inhibition similar to that observed in premixed flames.

7.   Measurement of the Induction Period Following Initiation

If the initiation of the combustion is not too "strong," i.e., if only a relatively small amount of energy is used to initiate the reaction, there will be an induction period between initiation and measurable propagation during which flame radicals (•H, •OH, etc.) build up at measurable rates. The length of the induction period is a function of both the strength of the initiation and the composition of the combustible mixture. Depending on the nature of the additive to the combustible mixture, the observed induction period may be longer (indicating inhibition by the additive), or may be shorter (indicating promotion of the combustion process by the additive).

In a variation on the propagation tube experiment, Erhard premixed volatile metal carbonyls with acetylene, oxygen, and amyl nitrate, and initiated the reaction photolytically; the amyl nitrate absorbed the photons from the flash lamp and served as an initial source of radicals and, to a lesser degree, as a fuel (Reference 21). In these experiments, the induction time (measured photometrically) was a measure of the rate of growth of •OH radical concentrations. Ni, Cr, Fe, and Mn carbonyls were found to decrease the induction time, thus indicating that they promote the combustion.

By contrast, Erhard and Norrish found that tetraethyl lead increased the induction time. This inhibition of the growth of •OH radical concentrations was proposed as the mechanism by which tetraethyl lead prevents knocking in internal combustion engines (Reference 22). Note especially that different metals may have different effects and that $Fe(CO)_5$, observed in other experiments to be an exceptionally effective inhibitor, promoted combustion in this experiment.

Shock-tube experiments, in which the heat at the shock front initiates the reaction, are similar. Matsuda and Gutman studied the effect of $Cr(CO)_6$ added to acetylene-oxygen-argon

10

mixtures using this technique and discovered that a chromium species (CrO_3 or perhaps CrO_2) was involved in the initiation chemistry, and shortened the induction time (Reference 23). These researchers further concluded that the chromium species was not involved in the main chain-branching chemistry.

8.   Afterburning Experiments

Afterburning experiments take advantage of the fact that hot fuel-rich mixtures, when mixed with fresh oxidizer, may ignite. In experiments by Vanpee et al. a fuel-rich mixture of ethylene, oxygen, nitrogen, and candidate powder was ignited in an explosion sphere; 80 ms later, the hot gases (2200 K) were allowed to escape through a fast-acting valve into fresh oxidizer, and the amount of powder required to reduce the afterburning flame duration to 50 percent of its uninhibited duration was measured (Reference 24). It was found that the most effective powders were those that vaporized and/or decomposed at relatively low temperatures and did not form refractory oxides as reaction products.

9.   Kinetics of Recombination Reactions

Several laboratories have explored the kinetics of recombination of flame radicals. All three of the obvious candidates have been targets of these studies:

$$H + H \rightarrow H_2 \tag{1}$$

$$OH + H \rightarrow H_2O \tag{2}$$

$$O + O \rightarrow O_2 \tag{3}$$

The work of Jensen, Jones, and Mace is representative (Reference 25). These researchers used spectroscopic techniques to measure the concentration of hydrogen atoms in the flame as a function of the concentration of potassium in premixed fuel-rich atmospheric H_2-O_2-N_2 flames, and concluded that (1) KOH is the catalytically active species in these flames and (2) the recombination reactions are homogeneous.

It should be noted here, as elsewhere in this report, that there is an extensive Russian literature on recombination of flame radicals, especially involving heterogeneous

11

reactions on the surfaces of entrained particles. Rate constants for these reactions have been published for particles of a variety of salts, especially alkali metal halides.

C.   EXTINGUISHMENT MECHANISMS

A single example will serve to illustrate the importance of understanding the details of extinguishment mechanisms (References 19 and 20). It has been known for at least 35 years that very small amounts of iron pentacarbonyl have a dramatic effect on flame speed. However, when the $Fe(CO)_5$ is added to the fuel stream of a counter-flow diffusion flame (with the flame front on the oxidizer side of the stagnation plane), the $Fe(CO)_5$ increases the strain rate, while when the $Fe(CO)_5$ is added to the oxidizer stream under the same conditions, the flame is inhibited. Clearly, to be able to take advantage of the possible advantages of related iron compounds, it is of vital importance to understand why the $Fe(CO)_5$ acts as an inhibitor under some circumstances and a combustion promoter under other circumstances.

1.   Particle Size

Very early in the effort to improve the effectiveness of dry chemical extinguishing agents, it was recognized that particle size is of vital importance. In their search for more effective explosion suppression agents for sheathed explosives, Dolan and Dempster explored a large number of candidate materials, and concluded that surface area is one of the dominant factors. For the most part, the materials that provided the most effective cooling of the hot gases were salts with large surface areas and decomposition temperatures below 200 °C (392 °F) (Reference 14).

Two years later, McCamy et al. described the results of a survey of several materials in diffusion flames. Of the powders tested, finely divided borax with 2 percent zinc stearate (to improve flow) ranked with the best of the agents tried, while borax (again with 2 percent zinc stearate) presented to the fire as coarse particles was among the least effective of the agents (Reference 6). Numerous other authors have commented on the importance of particle diameter and surface area; References 26, 27, and 28 are representative.

More recently, Ewing and coworkers made a careful study of the effect of particle diameter on the effectiveness of an agent (References 11 and 29). These workers began with the hypothesis that, for many materials, the extinguishing efficiency could be explained entirely in terms of thermal mechanisms. Particles that were larger than some "limiting" diameter were too large to vaporize completely and did not live up to their complete inhibition potential. To illustrate the results obtained by these workers, the limiting diameter for $K_2C_2O_4 \cdot H_2O$ was found to be 35 microns, while that of the less easily volatilized and fragmented K_2CO_3 was 14 microns.

The importance of particle size is not limited to compounds that inhibit combustion exclusively by thermal mechanisms. For compounds in which chemical catalytic mechanisms are operative, the size of the initial particle can significantly influence the concentration of catalytically active species in the flame.

Finally, it is noted that, while the size of a particle goes a long way toward determining the interactions of the inhibiting species at the microscopic level, the size of the particle also influences the deliverability of an agent, and its ability to penetrate a flame. The work of Altman et al. illustrates this point (Reference 10).

2.   Thermal and Catalytic Chemical Extinguishment Mechanisms

There has been considerable discussion over the years as to whether catalytic chemical mechanisms contribute to extinguishment, or whether the observed inhibition can be ascribed strictly to absorption of heat by the extinguishing agent. The underlying chemistry is well understood. Flame initiation reactions and some of the flame propagation and branching reactions are endothermic; moreover, many of these reactions have significant "activation" energies, which may be viewed as energy barriers that must be surmounted before the reactions can progress. Thus, there is a requirement for energy to flow upstream (into the unburned gases).

Although there are several mechanisms by which energy may be transferred upstream, the hydrogen atom is usually assigned the majority of the responsibility for upstream propagation of the flame. Of all the species in the flame, the hydrogen atom has the greatest average velocity, and hence is most likely to be able to diffuse significant distances upstream. In this context, the two possible mechanisms of inhibition are easily rationalized. (1) By cooling

the flame, one reduces the average kinetic energy of the H atoms in the flame, thus reducing the total number of hydrogen atoms with enough energy to overcome the activation energy barrier; it has been estimated that the minimum temperature necessary to sustain the propagation of a methane-air flame is about 1600 K (Reference 14). (2) Alternatively, one may imagine an inhibiting agent that interacts with radicals in the flame in such a manner as to reduce the number of H atoms in the flame. At some point, the rate of loss of radicals exceeds the rate of gain, and inhibition is observed.

With two possible mechanisms in mind, we shall first turn our attention to a more detailed description of thermal mechanisms, and then look at chemical catalytic mechanisms in some detail.

3.   Thermal Mechanisms

Several well-known thermal mechanisms are briefly described below:

a)   Thermal equilibration of the molecule (atom) with the flame

The amount of energy absorbed from the flame depends on both the temperature of the flame and the heat capacity of the molecule. The energy absorbed by a molecule increases its kinetic energy, causes it to rotate, and excites its vibrational modes. Since the number of vibrational degrees of freedom increases with the number of atoms (vibrational degrees of freedom = 3 × number of atoms - 6, for non-linear molecules), the heat capacity, and hence the ability of a molecule to absorb energy, increases with the number of atoms in the molecule. CO_2, for example, has a heat capacity of 54.3 J/mol-K at 1000 K, while CF_3Br has a value of 100.9 J/mol-K at the same temperature.

b)   Vaporization and sublimation

Vaporization is likely if the melting point of the agent is below the temperature of the flame, and (to a first approximation) the heat absorbed is taken to be the heat of vaporization at the normal boiling point. Some substances (KCl is an example) sublime directly from the solid phase to the vapor phase. For KCl, the energy absorbed during sublimation is about 370 kJ/mol.

14

c)   Dissociation

Weakly bound molecules may be dissociated by the thermal energy of the flame. Hydrates, for example, dehydrate with a concomitant absorption of energy from the flame. The carbonates decompose to yield CO_2 (Reaction 4), while the oxalates decompose to give CO and carbonates, which in turn decomposes to yield CO_2 (Reactions 5 and 6).

$$Na_2CO_3 \rightarrow Na_2O + CO_2, \quad \Delta H = + 322 \text{ kJ} \tag{4}$$

$$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO, \quad \Delta H = - 1359 \text{ kJ} \tag{5}$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \tag{6}$$
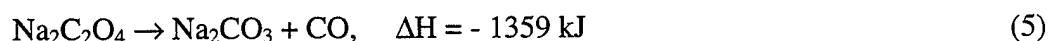
d)   Other mechanisms

Other mechanisms include fragmentation, deflagration of the particles, etc. Ewing and coworkers (References 11, 29, 30, and 31) have considered all of the available heat sinks for a large number of compounds and discovered that, with very few exceptions, the observed measures of extinguishment efficiency correlate very well with predictions based solely on consideration of thermal mechanisms. Representative data for n-heptane pan fires are displayed in Table 1 (Reference 11).

4.   Chemical Catalytic Mechanisms

Initial inklings that chemical catalytic mechanisms might be important arose from the simple observation that the effectiveness of many agents seemed to be disproportionately large compared with the heat capacities of these agents. Subsequently, Ewing and coworkers have shown that when one takes proper account of *all* of the available heat sinks, it is not necessary to invoke an explanation involving catalysis for many compounds. At the same time, Ewing et al. noted that there are *some* compounds for which the sum of all the thermal mechanisms *cannot* adequately account for the observed effectiveness, and it is necessary to consider additional mechanisms.

TABLE 1. EXTINGUISHMENT OF n-HEPTANE PAN FIRES.

Extinguishant	Amount Required for Extinguishment	
	Observed (mg/L)	Predicted (mg/L)
$K_2C_2O_4 \cdot H_2O$	33	33
K_2SO_4	34	29
NaCl	50	50
K_2CO_3	31	31
Na_2CO_3	43	41
$Na_2C_2O_4$	50	43
$KHCO_3$	35	35
$NH_4H_2PO_4$	54	50
Monnex	44	41
$K_4Fe(CN)_6 \cdot 3H_2O$	15	46

Regardless of the eventual evolution of the understanding of thermal mechanisms, several laboratories set out in search for evidence of catalytic mechanisms, and the accumulated evidence is overwhelming. Especially when one examines the details of interactions at the molecular level, it is quite clear that catalytic processes are operative in many cases. The $Fe(CO)_5$ system is particularly instructive. Ewing and others predict an extinguishment concentration of 38 mg of $Fe(CO)_5$ per liter in a premixed methane-air flame; this calculation takes into account all the possible heat sinks for this molecule and its fragmentation products (Reference 31). Experimental results obtained in NMERI laboratories are presented in Figure 1. The initial slope of the extinguishment curve is 1.8 mg/L, about 1/20 of the value predicted on the basis of thermal mechanisms. Clearly, no combination of thermal mechanisms can account for this initial behavior. (In fairness, it is noted that the concentration of $Fe(CO)_5$, which actually achieved extinguishment in the experiment illustrated by Figure 1 was 17 mg/L, a bit lower than the value [52 mg/L] listed by Ewing et al. (Reference 31). The difference between this experimentally measured value and the value derived from the initial slope of the curve in Figure 1 is one of the most interesting and important questions to be answered for the $Fe(CO)_5$ system.)
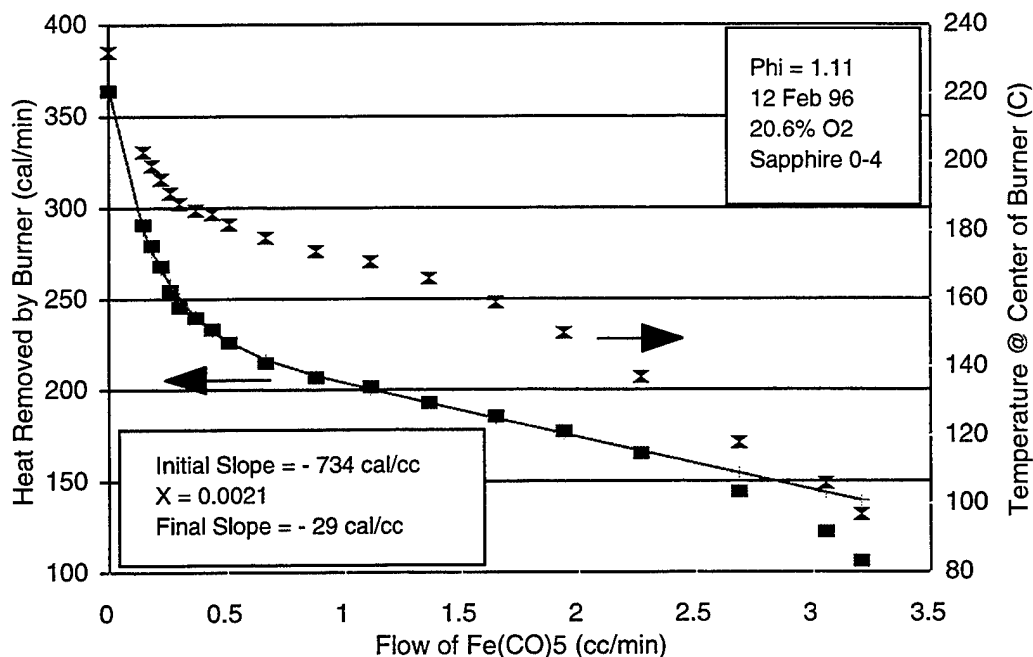
Figure 1. Inhibition of a Methane-Air Flame by Fe(CO)$_5$.

Since evidence has been found both for heterogeneous and homogeneous catalytic inhibition, each of these mechanisms is discussed separately in the following paragraphs.

5.   Heterogeneous Catalytic Recombination of Flame Radicals

Perhaps the most convincing piece of evidence in support of heterogeneous catalytic recombination of flame radicals is the observation that the particles have color temperatures considerably in excess of ambient temperatures in the flames. The chromium system is a case in point. Bulewicz and Padley reported that chromium oxide particles in fuel-rich, hydrogen-oxygen-nitrogen flames have color temperatures up to 500 K greater than the ambient flame temperature (Reference 32). The following mechanism is proposed.

$$Cr_2O_3(s) + H + H \ (or \ OH) \rightarrow Cr_2O_3(s) + H_2 \ (or \ H_2O) \tag{7}$$
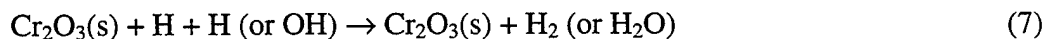
The "excess" temperature is greatest in lower temperature flames. The reaction is first order, and the rate determining step is the rate at which radicals strike the surface of the particles. This

finding was confirmed in other systems in another paper by Bulewicz and coworkers (Reference 33).

Heterogeneous catalytic recombination seems to apply to the magnesium oxide system as well. In an experiment in which magnesium was vaporized into an oxidizing atmosphere, a blue luminescence was observed both in the space above the magnesium furnace and on the surface of the MgO(s) deposited around the orifice of the magnesium furnace (Reference 34).

In other experiments, it has been observed that dust and other non-volatile materials such as talc, portland cement, silica, and fire clay (which have no appreciable volatility at flame temperatures) have some extinguishing capabilities (References 6 and 35). And finally, it should be repeated, that rate constants for recombination of radicals on salt particles have been measured and reported in the Russian literature.

6.   Homogeneous Recombination of Flame Radicals

While there are numerous examples of heterogeneous catalytic recombination of flame radicals, there are even more examples of apparent homogeneous catalytic recombination. The word "apparent" is used here because this conclusion is based largely on the observation that there seemed to be catalytic activity in systems where no particles were observed. Thus, for example, while Bulewicz and Padley ascribed extinguishment to heterogeneous recombination at high chromium concentrations in their flames, they were unable to observe any particles at lower chromium concentrations and, therefore, concluded that a homogeneous catalytic mechanism must be active (Reference 32).

a)   Halon 1301 (CF_3Br)

The classic (and perhaps most thoroughly studied) example of homogeneous catalytic recombination of flame radicals is Halon 1301 (CF_3Br). Following initial abstraction by an H atom, the Br atom is involved in a catalytic cycle, which results in the net recombination of H atoms.

$$CF_3Br + H \rightarrow CF_3 + HBr \qquad (8)$$

$$H + HBr \rightarrow H_2 + Br \tag{9}$$

$$Br + H + M \rightarrow HBr + M^* \tag{10}$$

In this set of reactions, M represents a third body, which removes part of the binding energy of the HBr and permits this reaction to go.

b)   Alkali metals

Among the metals, the most thoroughly studied are the Group IA elements: Li, Na, K, Rb, and Cs. In an early work, Rosser et al. studied the effect of very small (< 5 micron) particles of NaF, NaCl, NaBr, and other salts in premixed methane-air flames (Reference 36). It was found that these small particles were completely vaporized in the flames, and the researchers concluded that metal atoms are the important species. The proposed mechanism is represented as follows.

$$Na + OH + M \rightarrow Na\cdots OH + M^* \tag{11}$$

$$Na\cdots OH + H \rightarrow Na + H_2O \tag{12}$$

$$\text{Net Reaction: } H + OH \rightarrow H_2O \tag{13}$$

In related papers, Jensen and coworkers studied the effect of adding volatile sodium and potassium compounds to fuel-rich H_2-O_2-N_2 flames, and also concluded that metal atoms are the important species (References 25 and 37).

Further evidence for the role of metal atoms is found in two papers by Padley and Sugden, in which chemiluminescence by the metal atoms follows excitation involving homogeneous recombination of flame radicals (References 38 and 39).

$$H + H + Na \rightarrow H_2 + Na^* \tag{14}$$

$$Na^* \rightarrow Na + h\nu \tag{15}$$

$$H + OH + Na \rightarrow H_2O + Na^* \tag{16}$$

$$Na^* \rightarrow Na + h\nu \tag{17}$$

Padley and Sugden suggest that the mechanism is not limited to Group IA metals, but is operative as well for Mn, Fe, and other metals. In the case of Mn, it was commented that thermally excited emission of atomic Mn dominates in hotter flames, while the chemiluminescent emission is more important in cooler flames.

A differing view results from the experiments of Friedman and Levy (Reference 40). These researchers premixed sodium and potassium vapors with methane at temperatures up to 484 °C (903 °F), and introduced this mixture into a counterflow diffusion flame. It was found that concentrations of potassium vapor up to 3.5 mole percent did *not* influence flame strength. Consequently, metal atoms are not the catalytically active species. With this information in hand, and understanding that K and KOH are the only potassium species with appreciable concentrations in typical potassium doped flames, it was further concluded that KOH was the important species, and the following reactions were written.

$$KOH + H \rightarrow K + H_2 \quad \Delta H = -36.6 \, kcal \tag{18}$$

$$KOH + OH \rightarrow KO + H_2O \quad \Delta H = -13.7 \, kcal \tag{19}$$
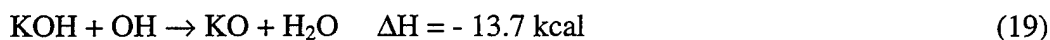
It was suggested that the salts, initially added to the flame, are first converted to K_2O, and that the formation of KOH follows.

$$K_2O + H_2O \rightarrow 2 \, KOH \tag{20}$$

Thermodynamic calculation indicates that the ratio of KOH to K at typical flame temperatures is higher in lower temperature flames.

$$@ \, 2222 \, K, \quad [KOH]/[K] = 2.6 \tag{21}$$

$$@ \, 2000 \, K, \quad [KOH]/[K] > 6 \tag{22}$$

This is consistent with the observation that catalytic chemical mechanisms seem to be more important in lower temperature flames.

This theme was further elaborated by Birchall (Reference 26). Birchall studied several potassium and sodium salts, both in co-flow and in counter-flow diffusion flames, using relatively large particles (70 microns). In this work, it was proposed that KOH is the active species and is formed by a slow, three-body process.

$$K + OH + M \rightarrow KOH + M^* \qquad (23)$$
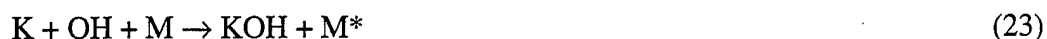
This, then is followed by removal of flame radicals.

$$KOH + H \rightarrow K + H_2O \qquad (24)$$

$$KOH + OH \rightarrow H_2O + KO \qquad (25)$$

$$KO + H + M \rightarrow KOH + M^* \qquad (26)$$

A variation on this theme was presented by Iya et al. based on work with fuel-rich premixed methane-air flames (Reference 13). The proposed mechanism invokes the formation of dipole-induced dipole complexes of metal atoms with $H_2O(g)$ molecules.

$$Na + H_2O + M \rightarrow Na\cdots H_2O + M^* \qquad (27)$$

$$Na\cdots H_2O + OH \text{ (or H or O)} \rightarrow NaOH \text{ (or NaH or NaO)} + H_2O \qquad (28)$$
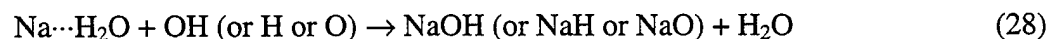
Schofield recently reviewed all the information presented to this point in the context of his own work (Reference 41). Schofield notes that flame stoichiometry plays a vital role in determining the key alkali metal species in the flame. In fuel-rich flames, the hydrogen atom concentration is large enough to suppress the concentrations of oxides and hydroxides, and the metal atom is the dominant species. The following catalytic cycle is proposed for recombination of flame radicals, using potassium as an example.

$$K + OH + M \rightarrow KOH + M^* \qquad (29)$$

$$KOH + H \rightarrow K + H_2O \qquad (30)$$

The first of these two reactions is quite efficient even though it is a three-body process.

For fuel-lean flames, on the other hand, there is a more complex chemistry involving: KOH, KO_2, KO, and K. The relative concentrations of these species in a typical fuel-lean flame at 1930 K are as follows: KOH (66%), KO_2 (31%), K (2%), and KO (1%). The following extinguishment cycle is proposed.

$$K + O_2 + M \rightarrow KO_2 + M^* \qquad (31)$$

$$KO_2 + OH \rightarrow KOH + O_2 \qquad (32)$$

$$KOH + H \rightarrow K + H_2O \qquad (33)$$
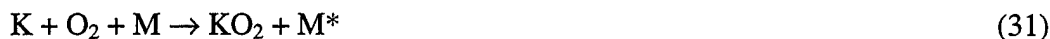
c)   Alkaline earth and other metals

In work with metals other than the alkali metals, there is almost universal agreement that the metal oxide (MO) is the important species. Much of the early work devoted to the study of the influence of metals on combustion involved the investigation of the mechanisms by which tetraethyl lead ($Pb(CH_2CH_3)_4$) prevents pre-ignition knock in internal combustion engines. In the work of Erhard and Norrish, mixtures of acetylene and oxygen were ignited photolytically, using a small amount of added amyl nitrate as a sensitizer (References 22 and 42). The length of the induction period (between the UV pulse and the onset of observable combustion) was taken as a measure of the rate of OH radical growth. Once the baseline had been established for the uninhibited system, tetraethyl lead was added and the experiment was repeated. It was found that (1) addition of tetraethyl lead increased the induction time (dark time); (2) the PbO concentration grew during the initial part of the induction period; (3) the PbO concentration decreased and the OH concentration grew rapidly near the end of the induction period; and (4) there was very little PbO left at the onset of observable combustion. It was concluded that PbO is the important species, the mechanism was homogeneous, and the following series of reactions was in consonance with these findings.

22

$$PbO + OH \rightarrow PbO(OH) \tag{34}$$

$$PbO(OH) + OH \rightarrow PbO_2 + H_2O \tag{35}$$

$$PbO_2 + R \rightarrow PbO + RO \tag{36}$$

Where R is a hydrocarbon radical

In a related study, but focusing on extinguishment, Vanpee and Shirodkar studied the effect of lead acetate, $Pb(OAc)_4$, and tetraacetylacetonatolead(IV), $Pb(acac)_4$, and other compounds, in counter-flow diffusion flames with a pool of ethanol as the fuel (Reference 43). Of all the compounds examined, the lead compounds proved to be the best, and the following mechanism was proposed to account for the specific interaction of the metal oxide with the flame.

$$PbO + H + M \rightarrow PbOH + M^* \tag{37}$$

$$PbOH + H \text{ (or OH)} \rightarrow PbO + H_2 \text{ (or } H_2O) \tag{38}$$
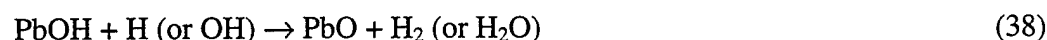
Here, the net reaction is recombination of H + H to give H_2, or of H + OH to yield H_2O.

Bulewicz and Padley proposed a similar mechanism to account for the apparent homogeneous catalytic inhibition of premixed $H_2 + O_2 + N_2$ flames at low concentrations (below the concentrations at which particles were observed) of $Cr(CO)_6$ and CrO_3 (Reference 32).

$$CrO + H + M \rightarrow CrOH + M^* \tag{39}$$

$$CrOH + H \rightarrow CrO + H_2 \tag{40}$$

The following variation has been cited by several workers to account for the observed inhibition of fuel rich $H_2 + O_2 + N_2$ flames; here, Ca is used as an example (References 44, 45, 46, and 47).

23

$$CaOH + H \rightarrow CaO + H_2 \tag{41}$$

$$CaO + H_2O\ (+\ M) \rightarrow Ca(OH)_2\ (+\ M^*) \tag{42}$$

$$Ca(OH)_2 + H \rightarrow CaOH + H_2O \tag{43}$$

Note that the second and third equations regenerate the CaOH from the CaO.

With respect to the mechanism outlined for Ca above, it is noted that both the first and third reactions are quite exothermic, and it would be anticipated that excited state CaO could result from the first, and excited state CaOH could result from the third. Indeed, in a similar study in which $MnCl_2$ was introduced into fuel rich $H_2 + O_2 + N_2$ flames by Padley and Sugden, both MnO and MnOH bands were observed in emission (Reference 39). Similarly, the FeO bands have been observed by numerous workers when iron compounds have been studied (References 18, 20, 21, and 48).

Most recently, Schofield reviewed the data for the Group IIA metals (Reference 41). As in the case of the alkali metals, the stoichiometry of the flame is of key importance. However, unlike the alkali metal case, the hydroxide, e.g., $Sr(OH)_2$, is the dominant species both for fuel-lean and for fuel-rich flames. In the case of the former, $Sr(OH)_2$ is the only really important species. For fuel-rich flames, $Sr(OH)_2$ dominates, SrOH and Sr are of secondary importance, and SrO is of even less importance. Schofield suggested that a catalytic cycle involving these four species should be able to explain inhibition by alkaline earth metal salts, but that attempts to date had not yielded satisfactory results.

7.   Relationship of Catalytic and Thermal Mechanisms

Having surveyed a great deal of the available information, it is useful to consider the relative roles of thermal and catalytic chemical inhibiting mechanisms. Unfortunately, this issue has somewhat polarized the research community. There is no question that thermal mechanisms contribute for all compounds, whether or not there is a chemical catalytic contribution. However, the proponents of catalytic-chemical mechanisms often seem to gloss over the fact that the recombination of flame radicals is quite exothermic. In some respects, the

effect of a catalytic recombination is to delay the heat release to a point farther downstream. Indeed, the increased temperature of some inhibited flames is evidence of this (Reference 31). It is useful to consider this observation in the context of the observation that the extinguishing efficiency of typical catalytic agents (such as $Fe(CO)_5$) is large for very small additions of agent, but diminishes as more agent is added (Reference 18). A plausible explanation invokes the possibility that, given the inherent ability of agents such as $Fe(CO)_5$ to absorb the released energy through thermal mechanisms, the ultimate extinguishing efficiency of these catalytic species at flameout would be less than, but not greatly less than, that predicted by purely thermal mechanisms (see especially References 11, 30, and 31). With this thought in mind, one returns to the question of how else energy might be removed from the flame. Radiative processes immediately come to mind, especially in view of the chemilumnescence observed in numerous systems and attributed to catalytic recombination of flame radicals. One also contemplates mechanisms by which energy might be prevented from reaching the initiation (pre-flame) zone, and the opacity of particles comes to mind. In this regard, one may consider soot, the aerosol particles introduced as extinguishing agents, and the aerosol particles generated due to reactions of the extinguishing agent in the flame (Reference 18).

D.   EXPERIMENTAL VARIABLES

To this point, the role of several experimental variables has already been implied; however, it is useful to consider a number of experimental variables explicitly. The remarkably diverse results will serve, once again, to indicate the exceptional complexity of inhibited flame systems. At the same time, they may provide clues that aid in unraveling this complexity.

1.   Role of Anions

While attention has been focused primarily on the role of the metal, numerous authors have noted that, for different salts of the same metal, the anion makes a difference. As a starting point, most authors agree with the following order of decreasing effectiveness (Reference 8):

oxalate > cyanate > carbonate > iodide >bromide > chloride > sulfate > phosphate

Dunderdale and Durie place five anions in a similar order (Reference 49).

hydroxide > carbonate > sulfite > chloride > sulfate

Several factors appear to be important.

a)   Ease of decomposition

Oxalates, for example, are relatively easily decomposed, which probably accounts for the observation that particles of these salts are relatively easily broken down into smaller particles with large surface areas and proportionately greater effectiveness.

$$C_2O_4^{2-} \rightarrow CO_3^{2-} + CO(g) \qquad\qquad (44)$$

b)   Catalytic effect of halogens

Quite apart from the metal, the Br and I atoms are known to catalyze the recombination of H atoms, as noted in the earlier discussion of Halon 1301 (CF_3Br). By contrast, the Cl atom binds too tightly to H, and is, therefore, not involved in a catalytic cycle. The same is even more true for the F atom.

c)   Volatility

For example, the potassium chloride (sublimes @ 1500 °C [2732 °F]) is more volatile than potassium sulfate (boiling point, 1689 °C [3072 °F]), which probably accounts for the greater effectiveness of the former.

d)   Tendency to form deposits

Dunderdale and Durie comment on the relative proclivity of anions to form deposits from the flame (Reference 49). Of the compounds examined by these authors, hydroxides had the smallest tendency to form deposits, while the sulfates had the largest tendency.

## 2.	Role of Additives

Several workers have noted that, when chlorine (or chloride) is added to the flame, the effectiveness of the metal is noticeably impaired. Birchall observed that, when halogen ions were added to the flames doped with potassium salts, the extinguishing effectiveness of the potassium ion was degraded significantly by Cl^-, less so by Br^-, and even less so by I^- (Reference 26). In similar experiments, Rosser et al. added CH_3Cl to Na_2CO_3- inhibited flames, and noted a reduction in the inhibition efficiency of the sodium carbonate (Reference 50).

Birchall proposed that the halogen removes some of the potassium ions from the flame by forming the relatively non-volatile potassium halide, and that the importance of this effect could be correlated with the strength of the K-X bond strength (K-Cl > K-Br > K-I). If one adopts the premise that it is the metal oxide, rather than the metal atom, that is the key extinguishing species, then one should compare the relative stability of the metal halide (e.g., KCl) with that of the metal hydroxide (e.g., KOH). Hastie compared several different metal halides, and noted that, since tin and antimony have relatively weak metal-chloride bonds, the extinguishing effectiveness of these metals might be less severely degraded (by comparison with K^+, for example) by the presence of chloride ions (Reference 8). In the case of antimony, it was found that the extinguishing effectiveness is actually enhanced by the presence of chloride ions. This synergistic benefit has been tentatively attributed to the fact that antimony chlorides are relatively volatile, and that formation of $SbCl_3$ would tend to prevent condensation of the antimony atoms from the flame zone.

## 3.	Role of Temperature

It is, of course, well known that the relative concentrations of key species in a flame change with flame temperature. It should, therefore, be of no surprise that the observations of one worker may be quite different from those of another, if the observations were made at different temperatures.

### a)	Lower limit for sustained combustion

Since the elementary first step in combustion of a hydrocarbon such as methane is endothermic and has a significant activation energy, it is not surprising that there is some flame temperature below which the upstream transport of energy is too small to sustain combustion. Dolan and Dempster estimate that a minimum temperature of 1330 °C (1600 K) is required to propagate flames in methane-air systems at atmospheric pressure (Reference 14). The limiting temperature found by Dewitte et al. is somewhat lower -- 1420 K (Reference 35).

b)   Increase in temperature with inhibition

As the inhibiting agent was added to the flame, it was observed in some instances that the flame temperature rose. This was observed early in the study of extinguishing agents such as Halon 1301, and attributed, at least in the case of cooled flat-flame burners, to the fact that the inhibiting agent causes the flame to lift off from the burner; with greater and greater lift off, less and less energy is extracted by the burner and the flame temperature approaches the adiabatic flame temperature (References 13 and 51). Fristrom noted that, under some circumstances, halogenated compounds are known to promote detonations; this phenomenon may be rationalized as follows (Reference 51). If the combustion is forced into a higher temperature regime, then more rapid combustion can be expected. Iya observed similar increases in the temperature of flames doped with $NaHCO_3$ and $Na_2C_4H_4O_6 \cdot 2H_2O$, and found a linear relationship between the temperature increase, Δt, and the concentration of sodium atoms in the flame (Reference 13).

c)   Effect of temperature on equilibrium

Temperature affects not only the equilibria of flame species, but also the equilibria of extinguishing species. As noted earlier, Friedman and Levy observed that the ratio of [KOH] to [K] in potassium-inhibited flames diminishes with increased temperature (Reference 40). Cotton and Jenkins studied inhibition by Group IIA metals and found that the inhibiting efficiency decreases with temperature, and that, above a temperature of about 2000 K, the catalytic extinguishment mechanism no longer competes effectively with the usual three-body recombination mechanisms such as the following (Reference 44).

$$H + H + M \rightarrow H_2 + M^* \hspace{4cm} (45)$$

These observations are consistent with the suggestion (discussed earlier) that the important catalytic species is the metal hydroxide molecule (such as CaOH). As the temperature of the flame is increased, [CaOH]/[Ca] decreases (due primarily to the fact that $\Delta S > 0$ for the dissociation of CaOH) in the same manner as [KOH]/[K] decreases.

A shift of equilibrium may also explain the reversal in the order of effectiveness as a function of temperature reported by Kim and Reuther (Reference 52). In stoichiometric premixed methane-air flames, these authors found the following orders of extinguishing effectiveness.

$$KHCO_3 > NaHCO_3 > NaCl, \text{ at } T > 1900 \text{ K} \hspace{2cm} (46)$$

$$KHCO_3 > NaCl > NaHCO_3, \text{ at } 1250 < T < 1900 \text{ K} \hspace{1.5cm} (47)$$

$$NaCl > KHCO_3 > NaHCO_3, \text{ at } T < 1250 \text{ K} \hspace{2cm} (48)$$
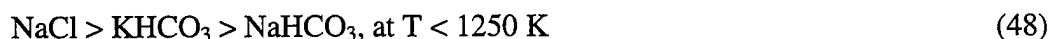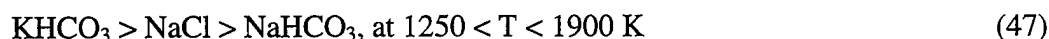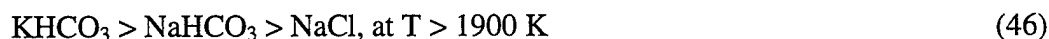
Finally, in the study of manganese doped flames by Padley and Sugden (Reference 39), thermal emission from atomic Mn dominated in hotter flames, while chemiluminescent contributions to the observed emission were more important at lower temperatures.

4.   Effect of Fuel-oxidizer Equivalence Ratio, ϕ

Several authors have examined the extinguishing effectiveness of metal-containing agents as a function of fuel-oxidizer equivalence ratio. Compounds specifically identified as being more effective in fuel-rich flames than in fuel-lean flames include $Fe(CO)_5$ (References 8 and 18), Na_2CO_3 (Reference 26), Al_2Cl_6 (Reference 53), and $SbCl_3$ (Reference 8). Miller et al. reported that most of the inhibitors investigated in their work were likewise more effective in rich mixtures than in lean mixtures (Reference 54).

Brabson and coworkers have studied the effect fuel-oxidizer equivalence ratio has on a wide spectrum of extinguishing agents. In this work, the heat absorbed by a flat-flame burner from a premixed methane-air flame with varying amounts of extinguishing agent was

studied as a function of the fuel-oxidizer equivalence ratio. Data for two physical extinguishing agents, CF_4 and HCF_3, are presented in Figure 2 and Figure 3 (Reference 55). Figure 2 compares the uninhibited flame with flames inhibited by the same amounts of CF_4 and HCF_3. It is immediately noted that HCF_3 removes very little heat from flames near the lower inflammability limit, while CF_4 extinguishes these flames. Conversely, moderately fuel-rich flames ($1.1 < \phi < 1.3$), are extinguished by HCF_3, and inhibited (but not extinguished) by CF_4. And finally, flames near the upper inflammability limit are extinguished by both agents.

Figure 3 plots these data in a different fashion, and illustrates the regions in which each·agent is the more effective. In this figure, the energy absorbed by the burner from an uninhibited flame is once again displayed. Superimposed for each agent is a data set, which shows the magnitude by which the agent reduces the amount of heat absorbed by the burner. It is evident from Figure 3 that CF_4 is nearly equally effective at all values of ϕ, while HCF_3 has very little effect on lean flames, but has a larger effect than CF_4 on rich flames. Brabson and others have proposed that these differences can be explained simply in terms of the "fuel content" of HCF_3.

Data for CF_3Br at several different concentrations are displayed in Figure 4. While this agent is somewhat more effective in fuel-rich flames, the effect is by no means dramatic. Nevertheless, the correlation between enhanced effectiveness in fuel-rich flames and the known extinguishment mechanism (catalytic recombination of H atoms) for this agent is worthy of note.

Results for $Fe(CO)_5$ are presented in Figure 5. Here, the enhanced effectiveness in fuel-rich flames *is* dramatic. At least three possible explanations can be offered.

a) "Fuel content"

Although the phenomenological result for $Fe(CO)_5$ is very similar to that for HCF_3, and although CO is a fuel, the amount of CO added to the flame is far too small. It is not possible to make the same argument for $Fe(CO)_5$ that one makes for HCF_3.
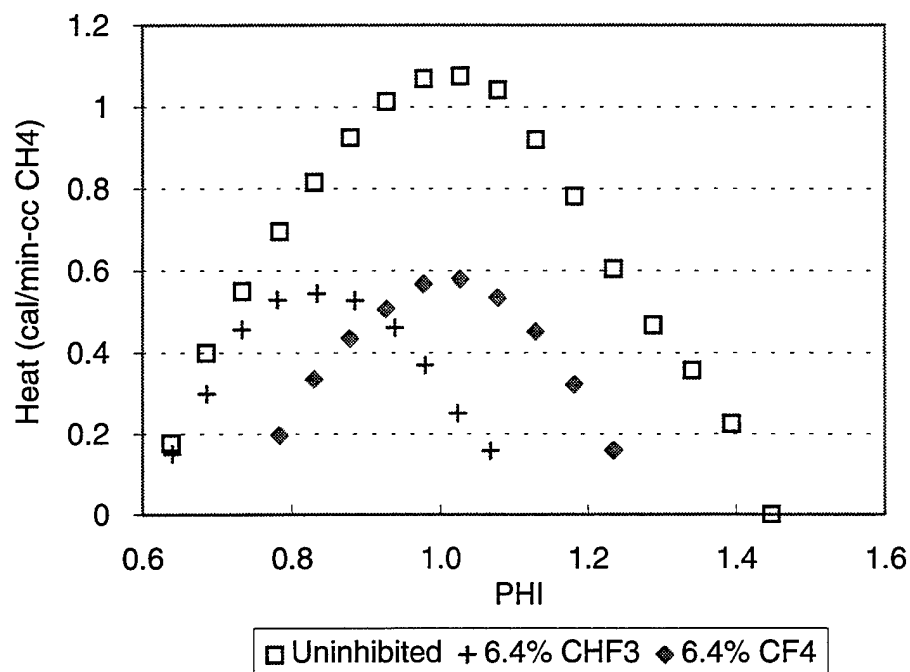
Figure 2. Heat Removed by the Burner.
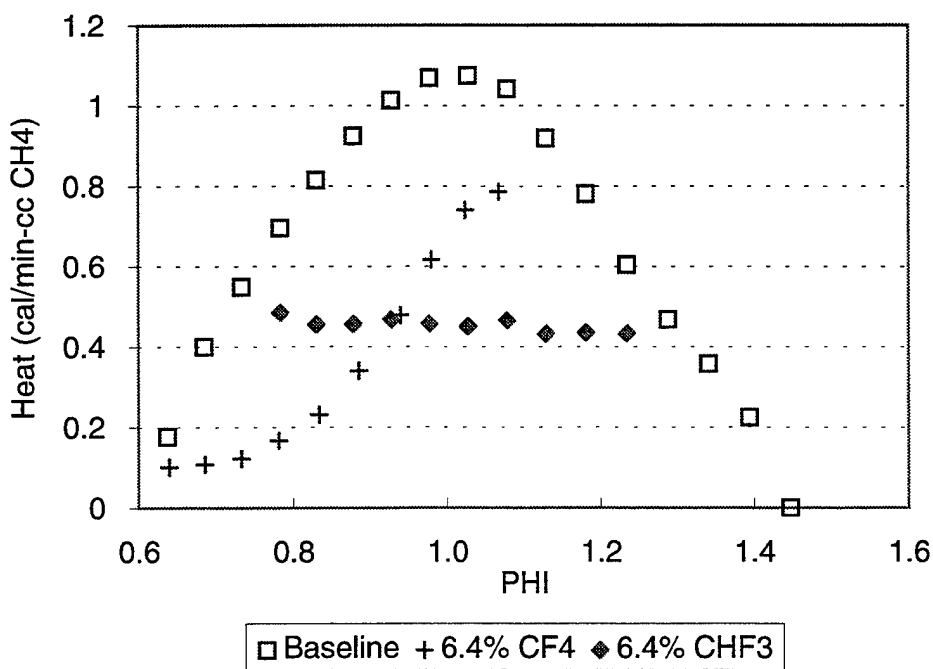
Figure 3. Reduction in Heat Absorbed by the Burner.
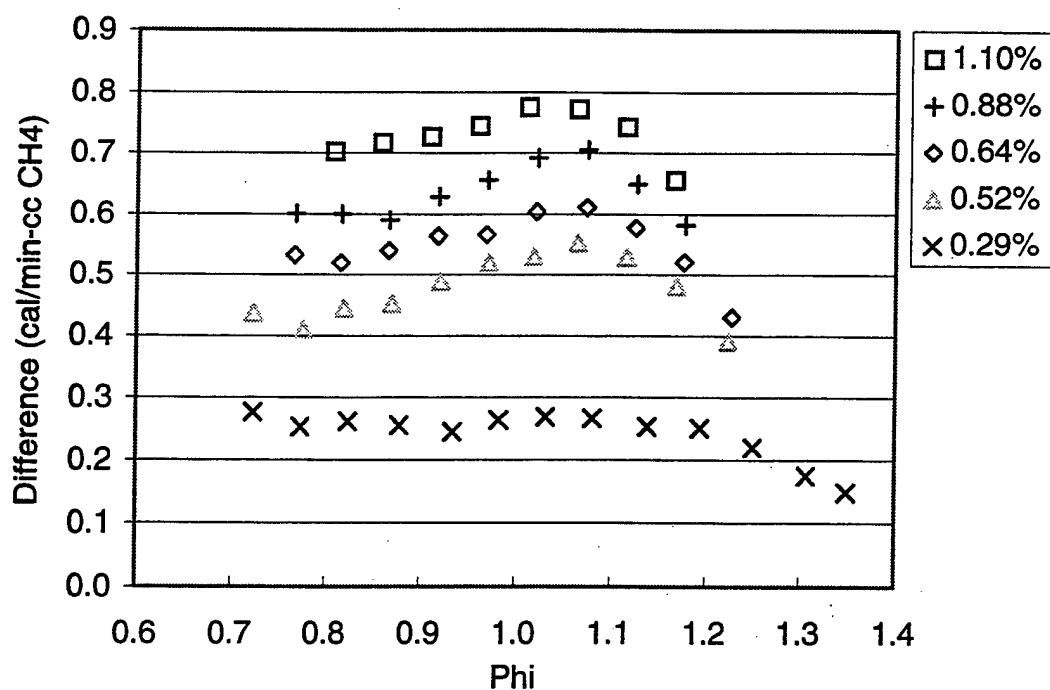
Figure 4. Halon 1301 Extinguishment Effectiveness.
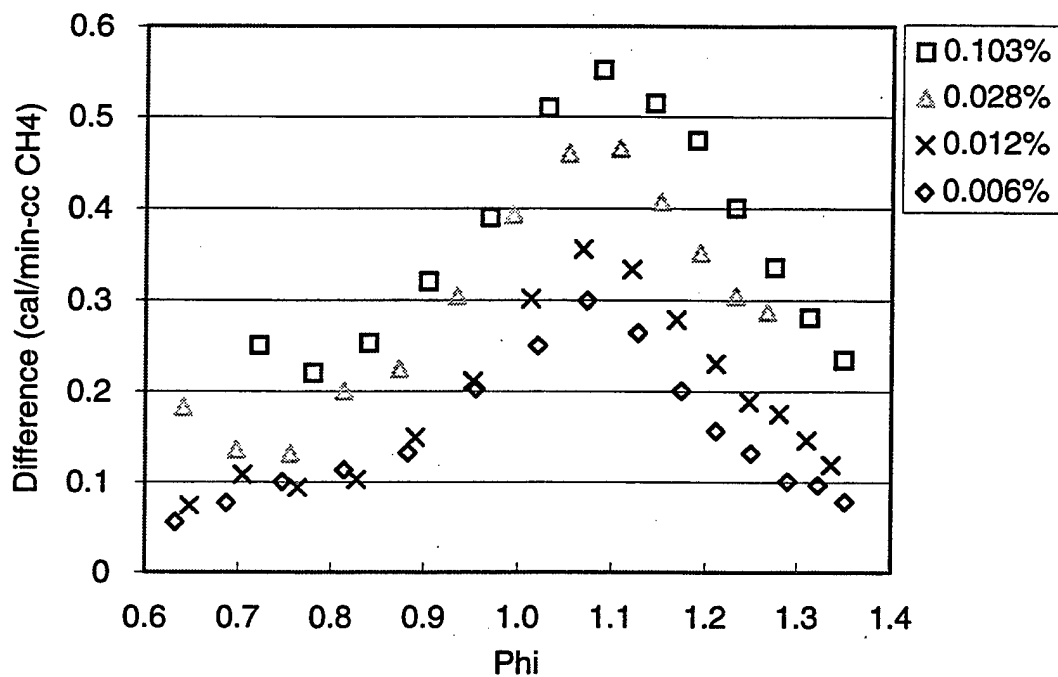
Figure 5. Fe(CO)$_5$ Extinguishment Effectiveness.

b)   Catalytic recombination of H atoms

Here, one would draw a parallel between the extinguishing mechanisms of CF_3Br and $Fe(CO)_5$.

c)   Catalytic oxidation of CO

The catalytic oxidation of CO is an overlay (on top of the extinguishment mechanism) and may account for the apparent additional heat release in fuel-lean flames.

In addition to the relatively large amount of information from premixed flame experiments, there are some important data from counterflow diffusion flame experiments. Linteris and Reinelt reported that the effect of $Fe(CO)_5$ on this type of flame is dependent on the stoichiometry of the flame and on the location of the flame with respect to the stagnation plane (References 19 and 20). With the flame on the fuel side of the stagnation plane, the $Fe(CO)_5$ has a negligible effect when added to either stream. When the flame is on the oxidizer side, addition of $Fe(CO)_5$ to the fuel stream results in an apparent promotion of combustion, while addition of $Fe(CO)_5$ to the oxidizer side results in inhibition similar to that observed in the premixed flame.

Another example of differences encountered in counterflow diffusion flames is reported by Milne and coworkers (Reference 56). The following extinguishment effectiveness relationships were observed when the halogenated agents were introduced on the air side and on the fuel side.

Air Side: $CF_3Br > CF_2ClBr >> CH_3Br$,
Fuel Side: $CF_3Br = CH_3Br$

These results are qualitatively consistent with the results reported by Brabson et al. for CF_4 and HCF_3 in premixed flames (Reference 55).

Miller also investigated the effect of adding the agents to both sides of a diffusion flame; in this work, methane was expanded into a (nearly) quiescent atmosphere of oxygen at a total pressure of 0.01 atm (Reference 57). Table 2 shows the mole percent required to achieve extinguishment.

TABLE 2. MOLE PERCENT REQUIRED TO ACHIEVE EXTINGUISHMENT IN
METHANE-OXYGEN FLAMES.

Additive	Added to fuel	Added to oxygen
N_2	6.0	13
BF_3	3.2	11
CCl_4	5.0	6.5
C_2HCl_3	15	8.1
CS_2	20	5.7
$POCl_3$	0.93	1.4

In summary, studies as a function of fuel-oxidizer equivalency ratio have yielded considerable information on the iron and on other systems; this information should provide both a basis for comparison with the results of detailed modeling and insight into the details of extinguishment by metal-containing agents.

5.   Catalytic Oxidation of CO

Given the potential importance of catalytic oxidation of CO (mentioned briefly above), it has been pulled out as a separate variable. In their shock-tube study of the acetylene-oxygen reaction, Matsuda and Gutman noted (1) that the reaction is accelerated by the presence of $Cr(CO)_6$ and (2) that the rate of CO oxidation is similarly enhanced by this compound (References 23 and 58). Hastie draws attention to this relationship and extends the discussion to Ni- and Fe-seeded flames (in which CO oxidation is accelerated) and to Pb- and Te-seeded flames (in which CO oxidation is retarded) (Reference 8).

6.   Role of the Fuel

While it is accepted that hydrogen, methane, and higher-hydrocarbon flames are significantly different, it is nevertheless useful to point out some examples. Thus, Wagner and coworkers found that $Fe(CO)_5$ more effectively inhibits hexane/air flames than hydrogen/air flames (References 16 and 48). Rosser and coworkers reported that 2.5 percent (w/w) $NaHCO_3$ was required to extinguish a stoichiometric propane/air flame, while a stoichiometric methane-

oxygen-nitrogen flame with the same initial velocity required only 1.0 percent (w/w) (Reference 50).

7.   Role of the Diluent

The concentration of the diluent has also been found to be important. Wagner and coworkers reported that $Fe(CO)_5$ is less effective in methane/oxygen flames than in methane/air flames (References 16 and 48). This may well reflect the importance of the diluent in carrying off the energy released by the catalytic recombination of the flame species.

8.   Role of Pressure

The fact that extinguishants are more effective at atmospheric pressure than at reduced pressures may also be related to the requirement to carry off the energy released by the recombination reactions. Thus, for example, Wagner and coworkers found that the effectiveness of $Fe(CO)_5$ falls off with decreasing pressure (References 16 and 48). In commenting on this observation, Hastie offers the suggestion that this may reflect the importance of a slow three-body reaction, perhaps the reaction by which the FeOH is initially formed (Reference 8).

$$Fe + OH + M \rightarrow FeOH + M^* \tag{49}$$

9.   Radiative Losses

Little attention has been given to radiative losses in most of the literature. However, given the very bright emission observed from the luminescent particles in Fe-seeded flames, it may be necessary to reconsider the role of radiative losses in providing a channel for cooling the very hot particles following catalytic recombination of flame radicals (Reference 18).

In contrast to the distinctly non-black body emission reported by Brabson et al., Bulewicz, Jones, and Padley observed a featureless emission, increasing smoothly with wavelength, for hydrogen-oxygen-nitrogen flames seeded with $UO_2(NO_3)_2$; the graph of log(I) versus λ paralleled the Wien's Law plot (References 18 and 33). Bulewicz et al. concluded that the observed chemiluminescence was due to recombination of flame radicals (•H and •OH) on

the surfaces of particles in the flames, and that the particles heated in this manner could be treated as gray bodies. A lively, but brief, dialog ensued in the literature (References 13 and 59).

McCamy et al. considered this issue from a different point of view (Reference 6). By measuring the opacity of flames inhibited by various dry powders, they estimated that less than 10 percent of the energy radiated in the direction of the fuel reaches the fuel; among the functions of the aerosol powder, then, is the reduction of preheating of the fuel due to direct exposure of the fuel to emitted radiation from the flame.

10. Practical Aspects of Particle Size

The importance of small particles (which completely vaporize/decompose) has been amply demonstrated in laboratory-scale experiments. However, there are some laboratory configurations in which very small particles may not even reach the combustion zone. Consider, for example, the counter-flow diffusion flame experiments by Birchall in which the powders were introduced into a down-flowing air stream (Reference 26). Birchall found that there was an optimum size for the particles. If the particles were too large, they fell rapidly through the flame and had only a small effect; conversely, if the particles were too small, they never penetrated the flame. The agents that scored best were those with long residence times in the flames and which disintegrated in this environment to yield a finely divided particulate smoke with particle sizes of about one micron.

Fristrom made similar observations and noted that the optimum particle size appears to be about 20 microns (Reference 51). Needless to say, most particles of this dimension are not completely vaporized/decomposed in typical flames, and the effectiveness of the agent is a compromise of the ability of the particle to penetrate to the combustion zone and the intrinsic extinguishing effectiveness of the active (molecular) species.

E. REVIEW OF RUSSIAN LITERATURE

For many years, the Russians have been interested in mechanisms by which solid aerosols extinguish fires. There is extensive literature on this subject, stretching from about 1970 to 1990; the material of primary interest seems to lie between 1970 and 1980. The principal author is

A. N. Baratov; however, he turned his interest to the halocarbons, especially Halon 2402, in the 1980s. Meanwhile, other authors picked up the study of reaction kinetics on well-defined surfaces such as carefully conditioned reaction vessel walls.

A search of Chemical Abstracts yielded the citations collected in Appendix B. This partially annotated list yields a sense of the research that has been done.

Table 3 identifies those papers that discuss flame inhibition by aerosols of specific salts. Additional papers in the annotated list no doubt have references to these salts; however, that information is not available at the present time (because only some of the papers are in hand). The numbers in Table 3 refer to entries in Appendix B.

TABLE 3. REFERENCES TO SALTS IN THE RUSSIAN LITERATURE.

Cation	F^-	Cl^-	Br^-	I^-	CO_3^{2-} HCO_3^-	$C_2O_4^{2-}$	$Cr_2O_7^{2-}$	SO_4^{2-}	PO_4^{3-} HPO_4^{2-} $H_2PO_4^-$
Li^+	1	1,13	1	1				19	
Na^+	1,3	1,3,8,13,19	1	1	3,6,10	3		3,6,8,12,19	
K^+	1	1,3,8,13,19	1,7	1,7	3	3	3	3,6,8,11,19	
Rb^+		1,13	1	1				6	
Cs^+		13						19	
Mg^{2+}								6	
Pb^{2+}								19	
NH_4^+					3,6				3,7

The following conclusions can be drawn from a review of the information in the annotated list in Appendix B.

(1) Heterogeneous recombination of radicals on the surfaces of the aerosol particles is well established and can be correlated with the degree of inhibition of a flame.

(2) The rate of recombination appears to be kinetically controlled (and not controlled by the rate of diffusion in the flame).

(3) The recombination efficiency depends, at least to some degree, on the nature of the aerosol particle. This suggests that the specific interactions of the radicals with the ions on the surface of the aerosol particles are important.

(4) There is no doubt much additional information can to be gained from a careful reading of the papers in the annotated list, especially those papers in the 1970 - 1980 time block. As a starting point, it is appropriate to translate several of the papers already in hand. In this regard, it should be noted that many of these papers appeared in relatively obscure journals, and that it has proved to be difficult to obtain some of the papers, let alone translations of them.

SECTION III

LABORATORY-SCALE EXPERIMENTS

A.   INTRODUCTION

More than a generation ago, it was discovered that very small amounts of iron pentacarbonyl have a dramatic effect on flames. Lask and Wagner reported that the addition of 0.017 percent $Fe(CO)_5$ to a stoichiometric hexane-air flame reduced the flame velocity by 30 percent (Reference 16). Stimulated by this initial result, Bonne, Jost, and Wagner extended the investigation of the inhibiting effect of $Fe(CO)_5$, and studied both methane-oxygen and methane-air flames (Reference 48). Here are some of the key findings of this latter work.

(1) $Fe(CO)_5$ more effectively inhibits hexane/air flames than hydrogen/air flames. Conversely, bromine is a more effective inhibiting agent in the latter than in the former; it is of interest to note that the •Br atoms are known to inhibit flames by catalytically recombining •H atoms.

(2) $Fe(CO)_5$ is less effective in methane/oxygen flames than in methane/air flames.

(3) $Fe(CO)_5$ is more effective in atmospheric pressure flames than in low pressure flames.

(4) By comparison with uninhibited flames, flames inhibited with $Fe(CO)_5$ have significantly lower •OH radical concentrations in the recombination zone, especially at distances greater than 2 cm above the burner in 60-torr flames.

(5) In flames inhibited with $Fe(CO)_5$, the concentration of Fe atoms peaks at about the same place as •OH, •CH and C_2 molecules (about 0.5 cm above the burner); the emission spectrum of iron atoms does not track with the concentration, peaks at a greater distance above the burner, about 1.3 cm, and falls off very slowly with increasing distance above the burner.

(6) The emission spectrum of the FeO molecule has two maxima in $Fe(CO)_5$-inhibited flames; the maximas are about 0.5 cm and about 3.3 cm above the burner.

Taken as a whole, these results suggest, but do not conclusively prove, that the mechanism of catalytic inhibition by $Fe(CO)_5$ may be different from that exhibited by the Br atom. Interesting candidates include •H + •OH recombination and even O + O recombination.

The effect of $Fe(CO)_5$ on premixed flames is being reinvestigated both at the National Institute of Standards and Technology (NIST) and in our own laboratories (Reference 60). Linteris and Gmurczyk recently reported a set of experiments in which premixed methane/air and propane/air flames were inhibited by $Fe(CO)_5$; these authors reported a 20 percent reduction in burning rate with an $Fe(CO)_5$ mole fraction of 24 ppm, but that, for $Fe(CO)_5$ concentrations above about 100 ppm, additional amounts of $Fe(CO)_5$ did not seem to be effective in contributing to further extinguishment of the flame.

More recently, the work on $Fe(CO)_5$ has been extended to include investigation of its behavior in counterflow diffusion flames (Reference 19). Results of this work were presented by Linteris and Reinelt at the Halon Options Technical Working Conference in May 1996 (Reference 20). These workers confirmed that the effect on a flame is quite dependent on the stoichiometry of the flame and on the location of the flame with respect to the stagnation plane. With the flame on the fuel side of the stagnation plane, the $Fe(CO)_5$ has negligible effect when added to either stream. When the flame is on the oxidizer side, the addition of $Fe(CO)_5$ to the fuel stream results in an apparent promotion of combustion, while the addition of $Fe(CO)_5$ to the oxidizer side results in inhibition similar to that observed in the premixed flame. These results with the counterflow diffusion flame add credence to the suggestion that the extinguishing mechanism involves the direct interaction of the $Fe(CO)_5$ with the oxidizer, and that the mechanism must be quite different from that exhibited by Halon 1301.

Although $Fe(CO)_5$ is too toxic to ever be used as a fire extinguishant, its testing has allowed insights into extinguishment mechanisms for transition metals. Based upon the efficiency of the $Fe(CO)_5$, other iron complexes and the remaining transition metal complexes are being investigated.

B. EXPERIMENTAL

1. Fe(CO)$_5$ Experiments

The Fe(CO)$_5$ work used the Sapphire 0-4 burner (an atmospheric burner) with the only modification being a separate nitrogen stream bubbled through Fe(CO)$_5$ in a gas saturator at room temperature. This stream was then mixed with the methane-air stream.

2. Synthesis of Hexafluoro-, Trifluoro-, and Acetylacetonatoiron(III)

The synthesis of the iron complexes followed the method outlined by Chaudhuri (Reference 61). Reagents used included "Baker Analyzed" reagent grade ammonium hydroxide, ferric chloride hexahydrate, and 98 to 99 percent solutions of the hexafluoro-acetylacetone, trifluoro-acetylacetone, and acetylacetone. The synthesis involved dissolving the ferric chloride hexahydrate in distilled water with warming, then adding ammonium hydroxide slowly while warming and stirring. Ferric hydroxide precipitated out and was digested for an hour on a steam bath to increase the crystal size so as to improve filtration. The ferric hydroxide was filtered and washed until free of chloride ions. The moist ferric hydroxide was then added to the appropriate acetylacetone, and again digested for an hour to form large red crystals upon cooling. The metal complex crystals were then filtered, washed with water, and dried. Yields of metal complex averaged 85 percent.

3. Hexafluoroacetylacetonatoiron(III) Experiments

The initial flame experiments with the iron acetylacetonates used the Sapphire 0-4 burner, described previously (Reference 62). The iron acetylacetonate sample was vaporized from a heated quartz sample cell placed between the incoming fuel-air line and the inlet of the burner (Figure 6). Experiments with this test apparatus demonstrated that Fe(acac)$_3$, Fe(tfac)$_3$, and Fe(hfac)$_3$ were able to inhibit and extinguish the flame, but there was no way to easily measure the amount of metal complex being delivered to the flame. Additionally, with the higher melting and boiling points of some of the metal complexes, condensation on the inside of the burner was a potential problem.

To Burner

Fuel and Air ⟶

Heating Coils

Insulation
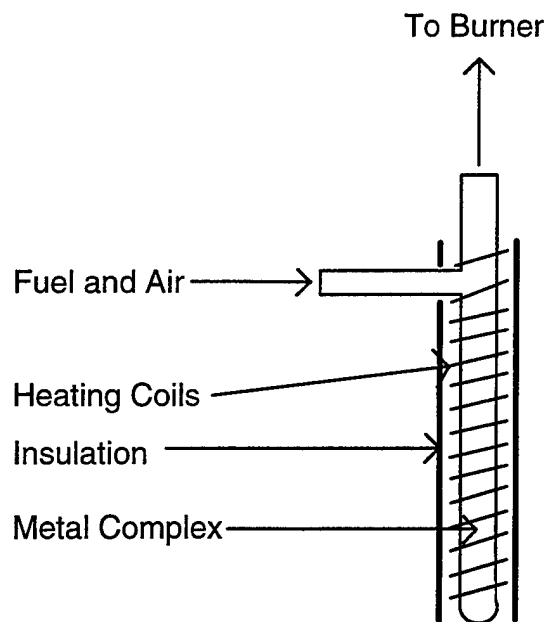
Metal Complex

Figure 6. Schematic Diagram of Heated Quartz Sample Cell.

To obviate potential condensation problems and enable measurement of the amount of metal complexes in the gas stream, a new insulated and heated burner was designed and built. Figure 7 and Figure 8 illustrate the key components of the experimental system. The Sapphire 0-7 burner is a modified laboratory Meker burner (diameter = 3.7 cm). The heat absorbed by the burner is carried off by ethylene glycol, circulated at a measured flow rate by a gear pump through a cooling loop (3/16" copper tubing) silver soldered to the outside of the burner rim. The increase in the temperature of the ethylene glycol is measured by a pair of thermocouples located in the cooling loop just below the points of attachment of the loop to the burner rim. The temperature at the center of the burner surface is sensed by a thermocouple spot-welded to the grid. The entire burner is insulated and resistively heated to prevent condensation of the slightly volatile extinguishing agents. A nitrogen sheath was used to minimize recirculation of the burned gases into the flame. Methane, "air" (21% O_2, 79% N_2), and the extinguishing agent were premixed. In typical experiments, the total flow rate was about 4000 cc/min (at 0.83 atm, nominal ambient atmospheric pressure in Albuquerque, New Mexico), and 200-500 calories/minute were removed from the burner by the coolant.
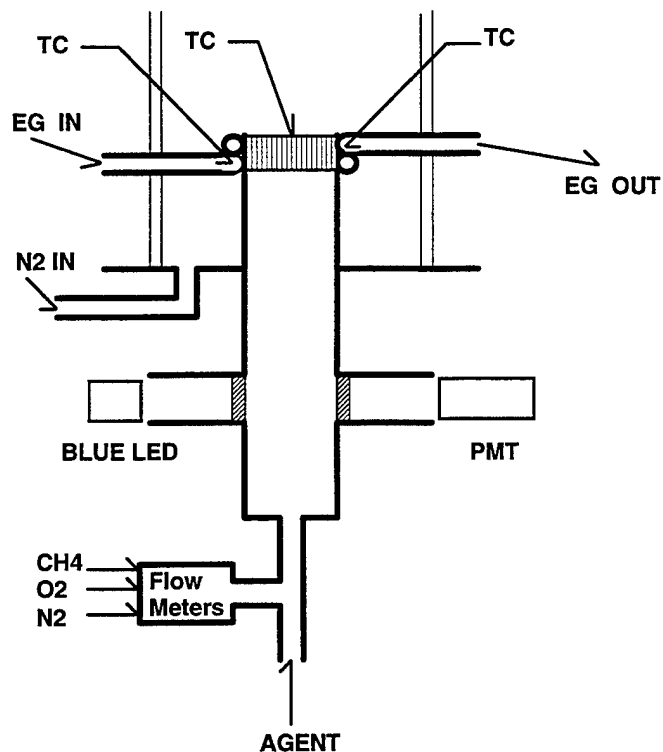
Figure 7. Schematic Diagram of the Sapphire 0-7 Burner.
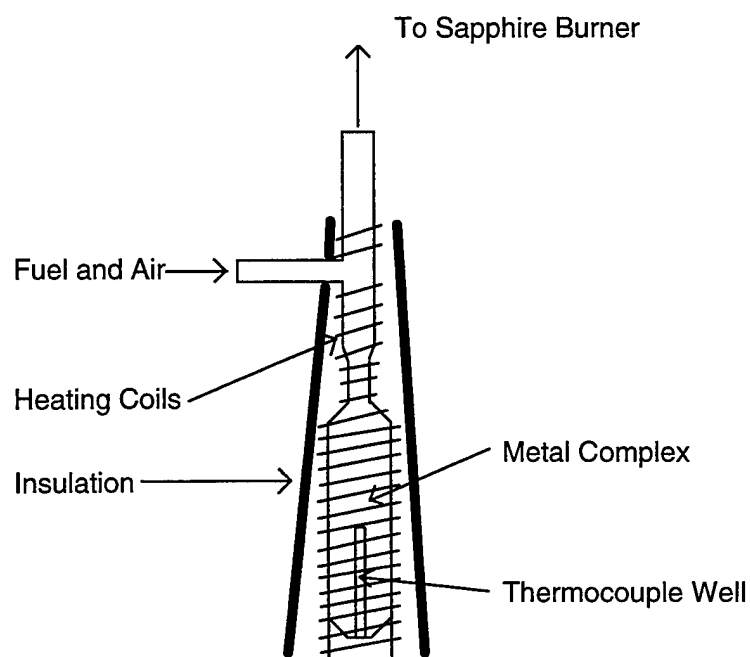
Figure 8. Heated Reservoir for Delivery of Metal Complexes to the Sapphire Burner.

An insulated, resistively-heated effusion cell containing the $Fe(hfac)_3$ was used to generate vapors of the extinguishing agent for mixing with the methane-air steam. The effusion cell temperature was set and maintained using an automatic controller with a thermocouple sensing element. Thermocouples on the outside of the cell and in a thermocouple well in the center of the sample reservoir were used for monitoring and controlling the cell temperature. A restriction was built into the upper part of the effusion cell to smooth the flow of gaseous iron acetylacetonate from the cell.

4. Spectroscopic Measurements of Metal Complexes

To explore the vaporization behavior of the three iron acetylacetonates, UV/visible spectra were made from 190 to 750 nm using a heated 5-cm gas cell in a Perkin-Elmer Lambda 3 spectrophotometer at several temperatures. The results showed that the Clausius-Clapeyron equation is obeyed by each compound in the temperature range of interest (Figure 9). The useful upper limit of temperature is near 162 °C, where $Fe(acac)_3$ decomposes.
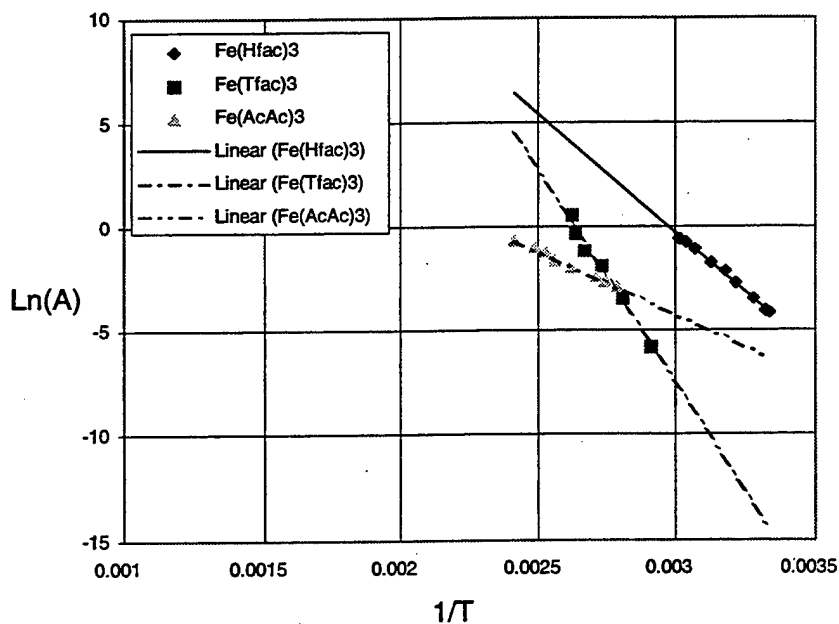
Figure 9. Spectroscopic Evaluation of Vaporization Behavior of
Iron (III) Metal Complexes at 430 nm.

Based on the above information, a new burner was designed with two optical windows, on opposite sides of the burner tube, about 4 cm below the flame-holding grid, that allow absorbance measurements in the O_2/N_2/fuel stream below the flame zone. The amount of Fe(hfac)$_3$ in the flame was determined by measuring the absorbance in the blue region of the spectrum. A blue LED was used as the light source, and a 1P28 photomultiplier with a cobalt blue glass filter was used as the detector. The molar extinction coefficient was determined in separate experiments with a heated 5-cm gas cell; the vapor pressure of Fe(hfac)$_3$ for this determination was taken from the work of Igumenov, Gerasimenko, and Morozova (Reference 63).

5. FeO Particle Size Measurements

With either the iron pentacarbonyl, Fe(CO)$_5$, or the metal complexes, Fe(acac)$_3$, Fe(tfac)$_3$, or Fe(hfac)$_3$, introduction of the compound into the premixed flame initially produced a bright yellow-orange color in the flame; at higher flow rates, luminous particles were observed. The bright yellow-orange color is due to emission by the FeO molecule (at wavelengths near those of sodium vapor). The luminous particles are believed to be agglomerated FeO molecules, possibly mixed with amorphous carbon (soot precursors). To explore the feasibility of characterizing these luminous particles in an active flame environment, the Sapphire 0-4 burner was installed in the Fraunhofer Diffraction Photometer, developed in our laboratories, and flames seeded with Fe(CO)$_5$ were briefly examined (Reference 64).

6. Extinguishment Effectiveness vs Volume Percent of Extinguishant Experiments

The amount of extinguishing agent was changed while all other flow rates were held constant; beginning with an uninhibited flame, extinguishing agent was added incrementally until flameout was achieved.

7. Extinguishment Effectiveness vs Fuel/Oxidizer Equivalence Ratio Experiments

The amount of methane was changed (thus changing the fuel-oxidizer equivalence ratio, ϕ) while all other flow rates (including that of the extinguishing agent) were held constant.

The fuel-oxidizer equivalence ratio was scanned incrementally from the lean inflammability limit to the rich inflammability limit.

8.　　Emission Spectra versus Fe(CO)$_5$ Content Experiments

Emission spectra were recorded with an f/4 Chromex 250FG Imaging Spectrograph equipped with a Photometrics CH-250 charged-couple-device (CCD) camera. The Imaging Spectrograph is a one-quarter meter instrument with a 300 lines/mm grating blazed at 600 nm. The CCD camera was passively air cooled to -25 °C, and had a range from 400 nm to 1000 nm. A seven-element optical fiber with a 1/2"-tip lens was used to collect the light and image it on the slit of the spectrograph. No attempt was made to resolve the emission as a function of location in the flame.

9.　　Laboratory Streaming Experiments

Limited streaming tests using the Laboratory-Scale Discharge Extinguishment (LSDE) apparatus discussed in Volume V of this report were carried out on Fe(acac)$_3$ and Fe(hfac)$_3$, using FC-5-1-14, HFE-449s1, and methanol as carriers for the metal complexes.

C.　　RESULTS

1.　　Vapor Pressure of Tris(hexafluoroacetylacetonato)iron(III)

For compounds that absorb radiation in a convenient spectral region, the absorbance can be used as a direct measure of the partial pressure of the compound in a gas-phase stream containing the compound.

The vapor pressure of liquid phase Fe(hfac)$_3$, has been measured from 343 K to 388 K (70 to 115 °C; Reference 63). The results are reported in the usual form, which tacitly assumes that the heat of vaporization is constant over the short range of the measurements (Equation 1).

$$\ln(p) = -\alpha/T + \beta \qquad\qquad [1]$$

Here, p is the pressure in atmospheres, α is the heat of vaporization expressed in Kelvin, T is the absolute temperature, and β is the intercept of the linear relationship. The reported values for α and β are 7199 K and 14.99, respectively (Reference 63).

The observed partial pressure is conveniently related to the absorbance through the ideal gas equation and Beer's law (Equation 2).

$$\ln(p) = \ln(nRT/V) = \ln(RTC) = \ln(RTA/b\varepsilon) = -\alpha/T + \beta \qquad [2]$$

Here, n is the number of moles, R is the gas constant (= 0.08206 atm-L/mol-K), V is the volume, C is the concentration expressed in moles/liter, A is the absorbance, b is the optical path length in cm, and ε is the molar absorptivity (extinction coefficient). Two useful forms can now be written (Equations 3 and 4).

$$\ln(AT) = \ln(b\varepsilon/R) + \beta - \alpha/T \qquad [3]$$

$$AT = p(b\varepsilon/R) \qquad [4]$$

From the first of these equations, it follows that a plot of ln(AT) as a function of 1/T should yield a straight line with a slope equal to $-\alpha$, and an intercept from which the molar extinction coefficient (ε) can be calculated (assuming that the value of β is known, as it is in this case). From the second of these equations, it is noted that, provided ε can be found, the pressure can be calculated from the observed value of A at any temperature. Needless to say, ε can be found by any experiment in which both A and p can be measured simultaneously.

In the first experiment, the Fe(hfac)$_3$ was contained in a 5-cm optical cell with Pyrex windows. A blue LED was used as the source, and a 1P28 photomultiplier with a cobalt-blue glass filter was used as the detector. A Kiethly electrometer was used to sense the output from the photomultiplier, and the output from the electrometer was transmitted directly to a strip chart recorder. The absorbance was calculated in the usual manner from the relative radiant power values recorded. With very little effort, it was possible to select a set of operating

parameters such that the optical system was virtually insensitive to changes in ambient light in the room.

Figure 10 displays the experimental data. The equation from Reference 63 was used to calculate the vapor pressure at each temperature. It must be noted that this equation applies only to those data for which the sample is above its melting point, reported to be 49 °C (120 °F) (Reference 65). These are the six highest temperature points in our data. Accordingly, the data for these six points were fitted to a linear equation of the form described above, and the value of the molar extinction coefficient (ε) obtained from the slope is 3600 M^{-1} cm^{-1}. It was observed that the least-squares line did not pass through the origin (although it should do so), which suggests that the true value of ε is likely somewhat larger than 3600, and probably closer to 4000 M^{-1} cm^{-1}. Nevertheless, we now have in hand a reasonably good value of ε, which can be used to calculate the partial pressure of Fe(hfac)$_3$ at any temperature, regardless of the physical state (solid or liquid) of the sample with which the vapor is in equilibrium.
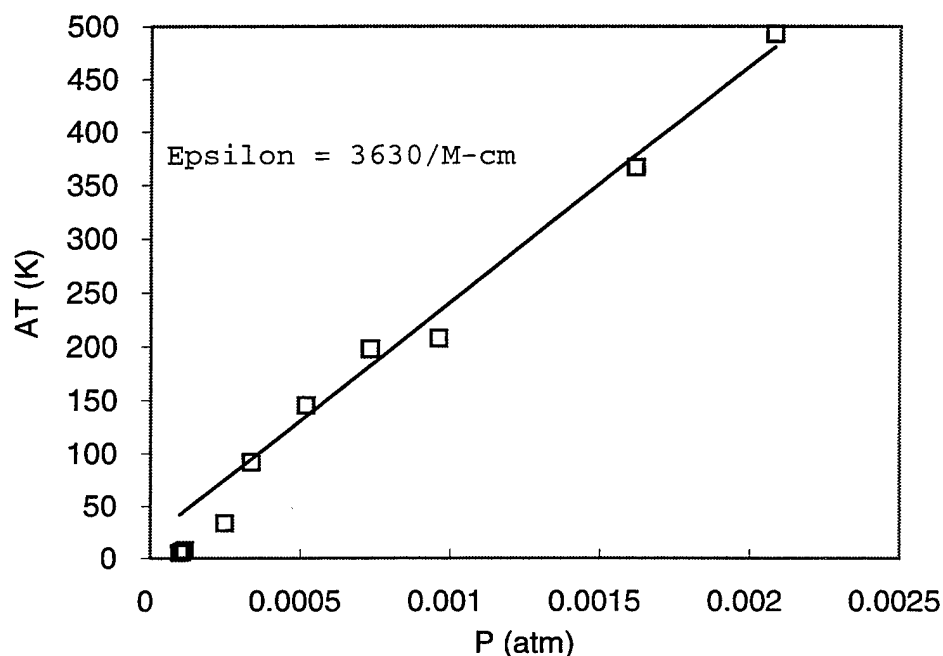
Figure 10. Beer's Law Plot for Tris(hexafluoroacetylacetonato)iron(III).

Figure 11 displays the data plotted in a different manner. Here, the slopes of the two lines are the heat of vaporization of the liquid (higher temperature data) and the heat of sublimation of the solid (lower temperature data). The intersection of the two lines is the melting point. Comparison of these data with the literature values gives considerable insight into our experiment. Slope(2), the heat of vaporization of the liquid, is about 13 percent lower than the literature value, and the melting point of the sample is about 7 °C below the reported value. Moreover, it is evident that there is considerable scatter in the data. However, the essential correctness of the results is strong confirmation of the validity of the experiment and of its value in yielding vapor pressure data for the region (below the melting point of the sample) where no data are available in the literature. Even with these data in their present state (and they warrant refinement), vapor pressures of $Fe(hfac)_3$ should be estimable to within ± 20 percent.
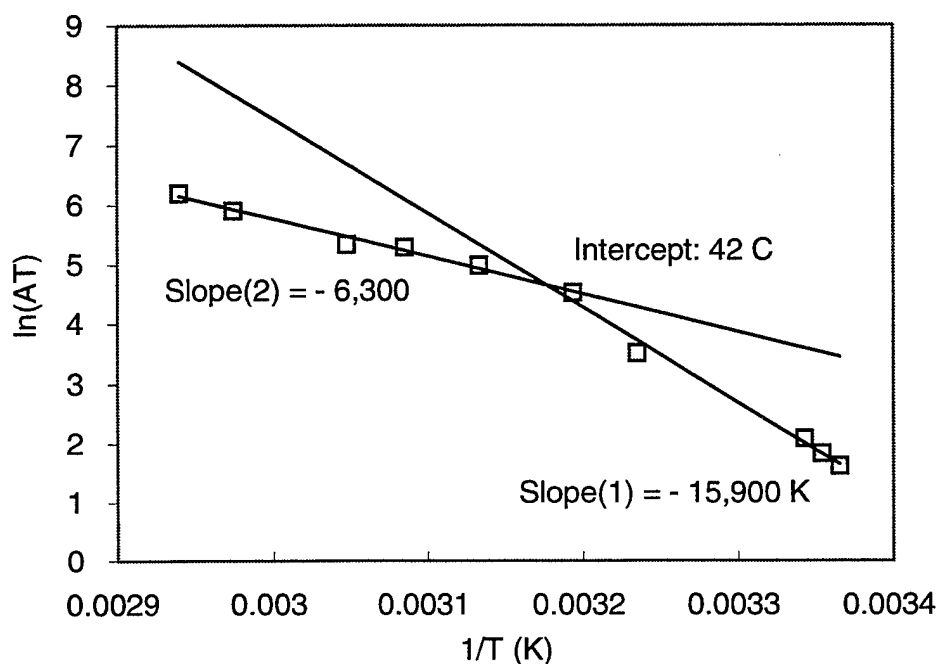
Figure 11. Absorbance as a Function of Temperature for Tris(hexafluoroacetylacetonato)iron(III).

2. Catalytic Extinguishment

The experiment that most convincingly demonstrates that the iron-containing extinguishants catalytically inhibit the flame is the experiment in which the heat removed by the burner (HRBB) is studied as a function of the amount of extinguishing agent added to the premixed gases. A typical result is shown in Figure 12. In this typical data set, the HRBB shows a precipitous drop for the first few incremental additions of agent, followed by a linear decrease, and terminated by extinguishment (flameout). The data are easily treated by first fitting data for relatively large flow rates to a linear equation, and then fitting the residual data for small flow rates to an exponential equation of the form $y = a + b\,e^{-cx}$. The exponential form of the behavior at small flow rates is characteristic of catalytic quenching.

For comparison with data for other agents (a physical agent and a catalytic agent), Figure 13 illustrates results typical of a physical extinguishing agent, while Figure 14 shows results typical of a catalytic chemical extinguishing agent. Note especially the straight line exhibited by the nitrogen and the exponential curve displayed by the Halon 1301. The slope of
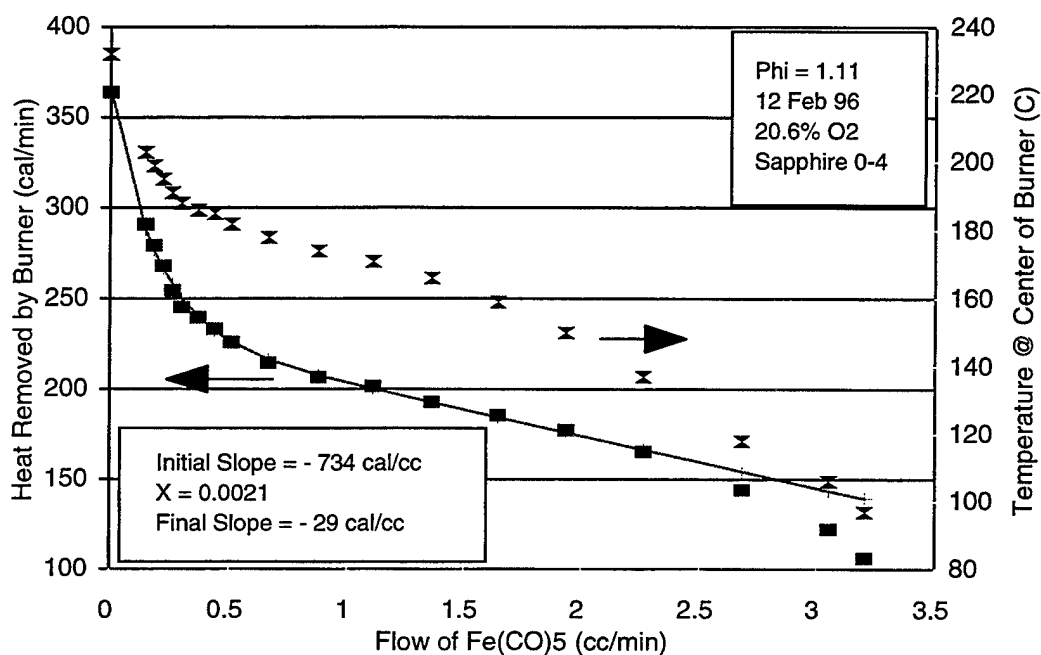
Figure 12. Inhibition of a Methane-Air Flame by $Fe(CO)_5$.
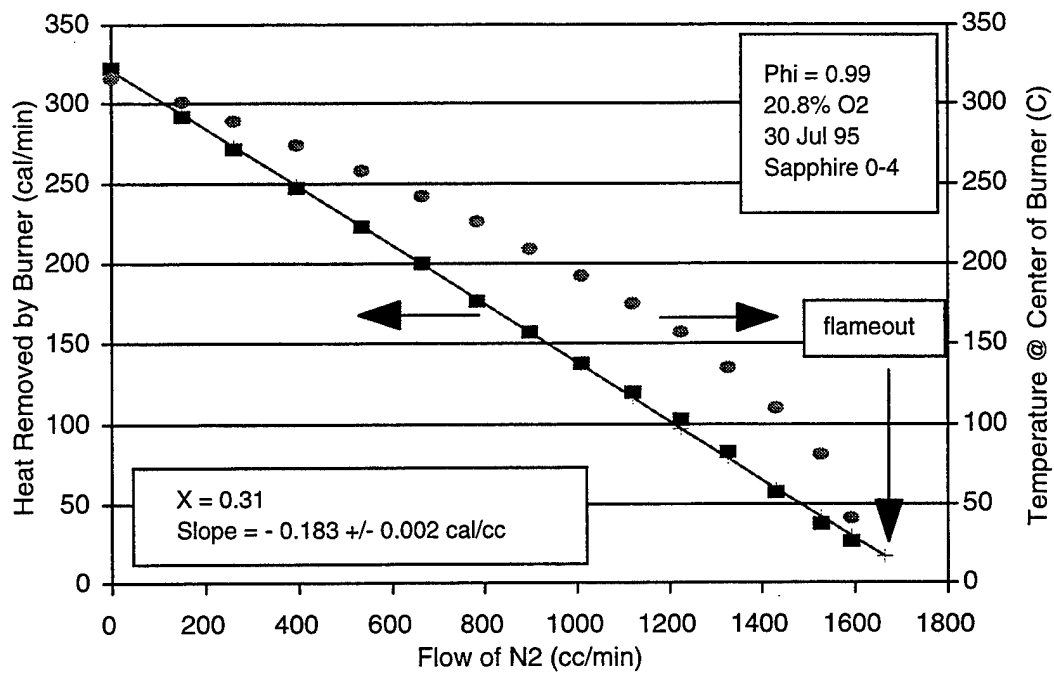
Figure 13. Inhibition of a Methane-Air Flame by N_2.
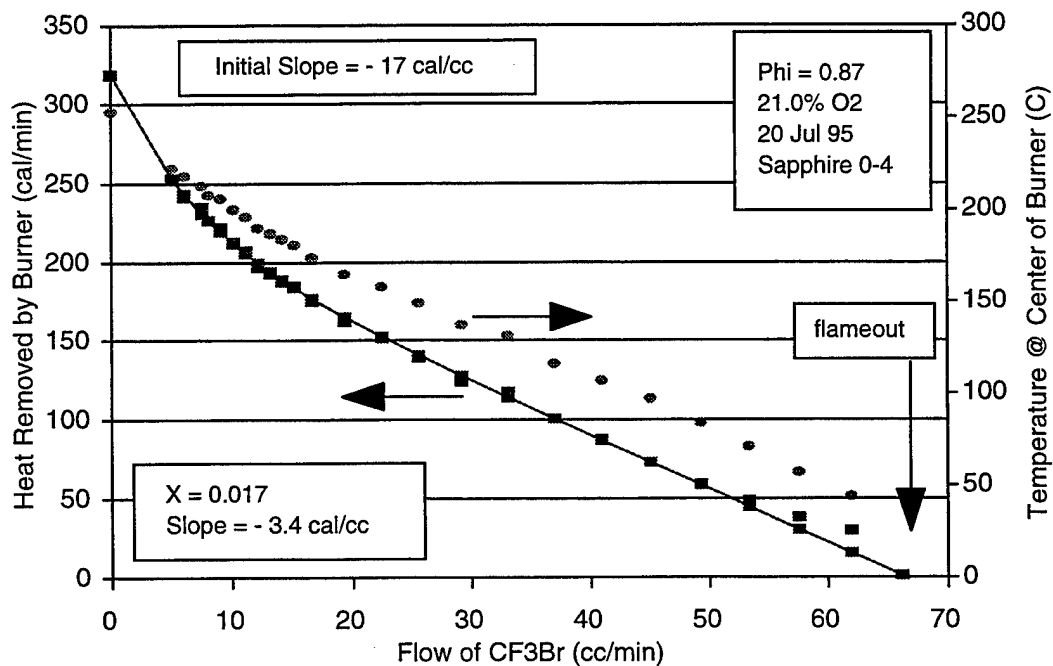
Figure 14. Inhibition of a Methane-Air Flame by Halon 1301.

51

the curve at any point is a measure of the effectiveness of the agent at that point. The following, essentially meaningless, calculation illustrates the dramatic effect that small amounts of $Fe(CO)_5$ have on the flame. From the initial slope, and the fact that about 20 percent of the total heat in the flame is removed by the Sapphire 0-7 burner, it can be estimated that the impact on the reduction of the heat in the flame is on the order of 4×10^5 kJ/mol $Fe(CO)_5$. (For comparison, the heat of complete *atomization* of $Fe(CO)_5$ is only 6.0×10^4 kJ/mol.) Even with the final slope of -29 cal/cc, the effectiveness of this iron-containing compound is quite significant. (For comparison, if one dissociates the $Fe(CO)_5$ into Fe(g) and CO(g) and adds the energy required to bring these gas-phase species to a temperature near that of the flame, one would expect to observe a slope of about -6 cal/cc.)

It should be noted, in this regard, that extinguishment was routinely observed in $Fe(CO)_5$ experiments. Typical $Fe(CO)_5$ volume percentages at which extinguishment was observed ranged from 0.05 to 0.08 percent. In the experiment illustrated by Figure 12, the higher flow rates of $Fe(CO)_5$ resulted in significant buildup of deposits on the surface of the burner; these deposits doubtless insulated the burner and caused the HRBB to be smaller than it would have been in the absence of these deposits. In this regard, note the "tail-off," beginning with an $Fe(CO)_5$ flow rate of 2 cc/min.

3.   Effect of the Carbonyl Moieties

To examine the possible effect of the CO fragments on the overall extinguishment effectiveness, the concentrations of all the gases except methane were fixed, and the fuel/oxidizer equivalence ratio, ϕ, was "scanned" by varying the flow rate of methane from the lean inflammability limit to the rich inflammability limit. The results of a typical experiment are shown in Figure 15. As expected, the HRBB for the uninhibited flame has its maximum at the stoichiometric ratio. By contrast, the peak for the inhibited flame is on the fuel-lean side (and the peak of the difference curve is on the fuel-rich side). Thus, it is clear that, while the $Fe(CO)_5$ contributes to the net extinguishment of the flame at all values of ϕ, it extinguishes fuel-rich flames more effectively than fuel-lean flames. This is reminiscent of experiments in which extinguishment by CF_4 was compared with extinguishment by HCF_3 (Reference 55). In the CF_4/HCF_3 experiments, it was concluded that the HCF_3 has some fuel value. When ϕ was

52

adjusted for the amount of O_2 required to react with the H in the HCF_3, it was found that the HRBB curves for the two compounds were nearly superimposable, lending credence to the hypothesis concerning the fuel value of the HCF_3. In the same vein, it is tempting to attribute the observations in the $Fe(CO)_5$ experiments to the "fuel value" of the CO moieties. A difficulty arises, however, when one realizes that the shift in the peak of the HRBB curve is quite significant, and not commensurate with the very small amount of CO actually contributed to the flame by the added $Fe(CO)_5$. Thus, the most that can be said is that the $Fe(CO)_5$ "promotes" the combustion in the fuel-lean regime, while contributing to the overall extinguishment of the flame. However, as noted elsewhere in this report, some metal-containing species are known to catalyze the oxidation of CO in flames, which may explain the apparent "promotion" of combustion in the fuel-lean flames.

Figure 16, the plot of Fractional Effectiveness (defined as the ratio of the reduction in HRBB divided by the total amount of heat in the uninhibited flame), yields the same message. Note that the $Fe(CO)_5$ is about twice as effective in fuel-rich flames as in fuel-lean flames.

The sharp contrast between the results of these premixed flame experiments with the results for the counterflow diffusion flame experiments is especially important. In the premixed flames, inhibition is observed at all mixture ratios, but is especially important in fuel-rich flames. In the diffusion flames, strong inhibition is observed only when the $Fe(CO)_5$ is introduced from the oxidizer side *and* the flame is on the oxidizer side of the stagnation zone. Taken together, these results sharply limit the number of mechanisms that can be proposed for inhibition by the metal species. The results are consistent with FeO as the active species, and suggest that the FeO molecules inhibit the flame chemistry by removing an oxygen rich species from the flame. Clearly, a detailed understanding of the comparative results obtained with the premixed and diffusion flames will go a long way toward elucidating the inhibition chemistry.

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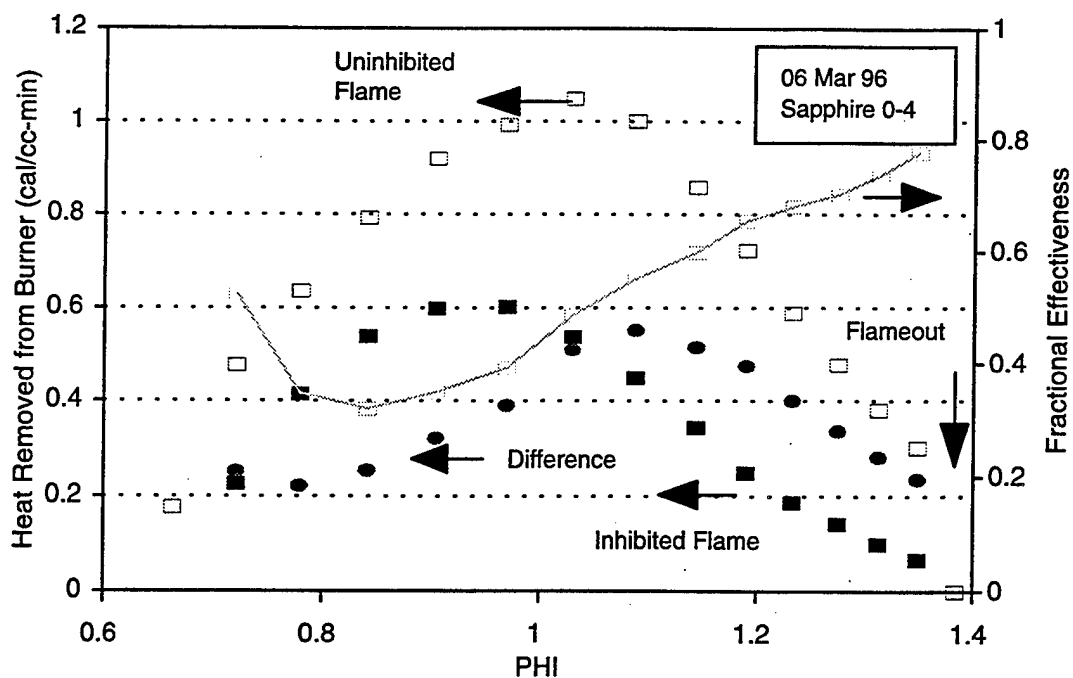
Figure 15. Inhibition of a Methane-Air Flame by 4.00 cc/min Fe(CO)$_5$.
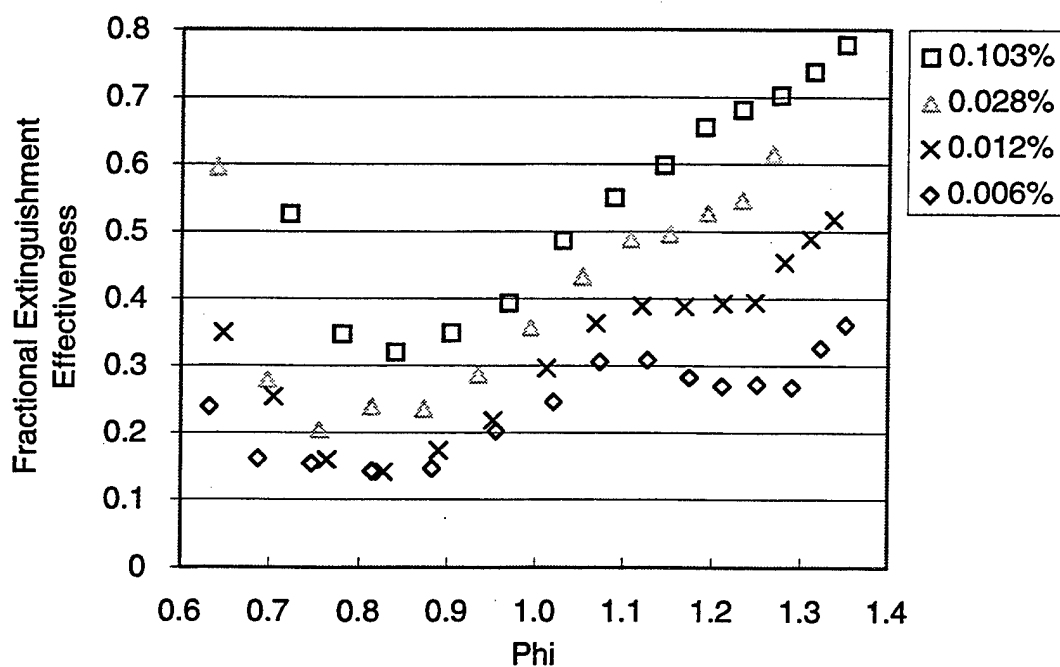
Figure 16. Fe(CO)$_5$ Fractional Extinguishment Effectiveness.

Figure 16 and Figure 17 compare the results for $Fe(CO)_5$ at several different concentrations. Figure 17 illustrates the effectiveness of $Fe(CO)_5$ by plotting the decrease in heat absorbed by the burner as a function of ϕ, while Figure 16 collects the fractional effectiveness data for the same experiments. It is especially instructive to compare the results in Figure 17 with a similar set of results for a typical physical extinguishing agent such as CF_4 (Figure 18). Note that, in the experiments with CF_4 (a typical physical extinguishing agent which reacts chemically with the flame only reluctantly), the magnitude of the reduction in the heat removed by the burner is nearly independent of ϕ. While the decrease in heat absorbed by the burner is essentially independent of ϕ for CF_4, the distinct peak near $\phi = 1.1$ for the $Fe(CO)_5$ is clearly indicative of the catalytic quenching mechanism at work in this compound. It may be necessary to obtain detailed concentration profiles (by mass spectrometry and other techniques) and model the system with a complete kinetics model in order to completely elucidate the implications of these findings. However, it is interesting to observe that CF_3Br (which catalytically recombines •H atoms, as noted above) displays a similar, though not as marked, maximum near the same value of ϕ (Figure 4).
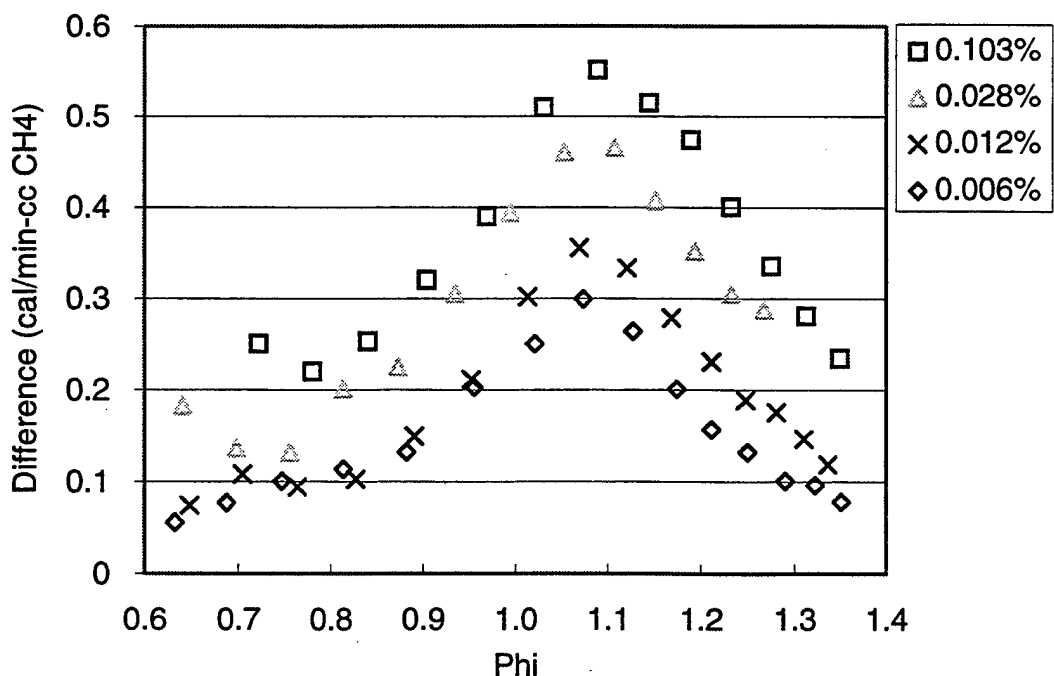
Figure 17. $Fe(CO)_5$ Extinguishment Effectiveness.
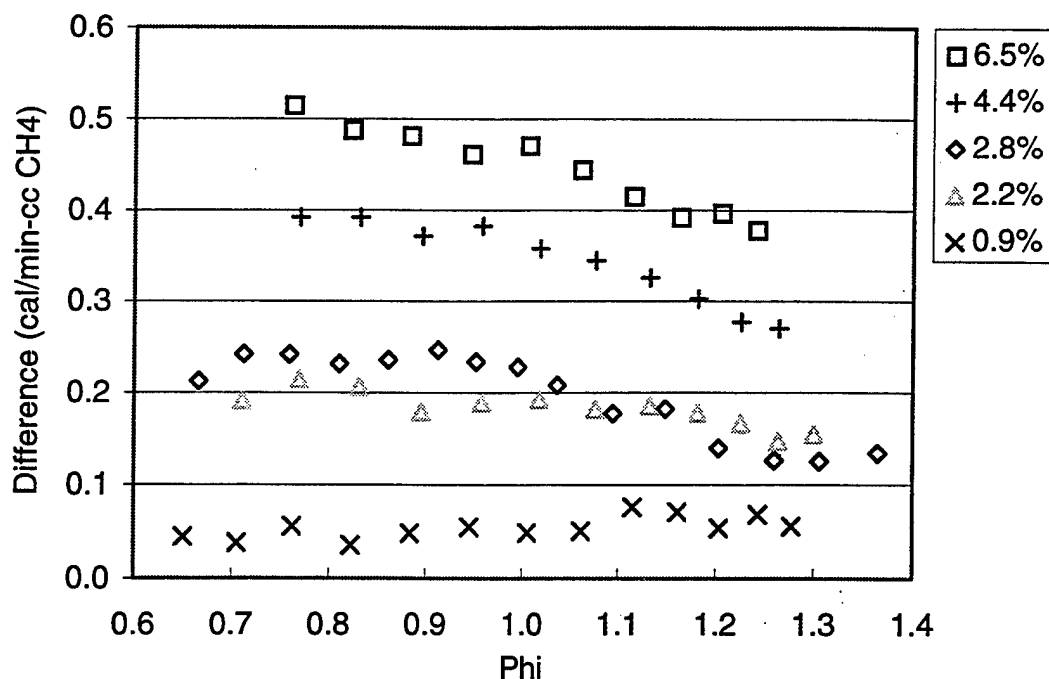
Figure 18. CF$_4$ Extinguishment Effectiveness.

The requirement for a set of follow-on experiments with a compound lacking the CO moieties is clearly indicated. Although initial experiments with Fe(hfac)$_3$ have been completed, the critical experiments (in which the HRBB is studied as a function of ϕ for a fixed amount of Fe(hfac)$_3$ have not yet been done.

4.   Fe(hfac)$_3$ Experiments

To date, experimental work with Fe(hfac)$_3$ has focused on experiments in which the HRBB was studied as a function of amount of agent added to the flame. A typical result is illustrated in Figure 19. It is immediately apparent that the results are nearly identical with those for Fe(CO)$_5$, clearly indicating that the iron in the agent is involved in the inhibition. While the slopes of the curves are greater than those for Fe(CO)$_5$, it should be noted that small experimental uncertainties can lead to large uncertainties in these slopes; therefore, the significance of these differences remains to be seen. One experimental difficulty was encountered in these experiments: to date, it has not been possible to take the experiment to flameout. This may be a consequence of thermal decomposition of the Fe(hfac)$_3$ at the higher effusion cell temperatures

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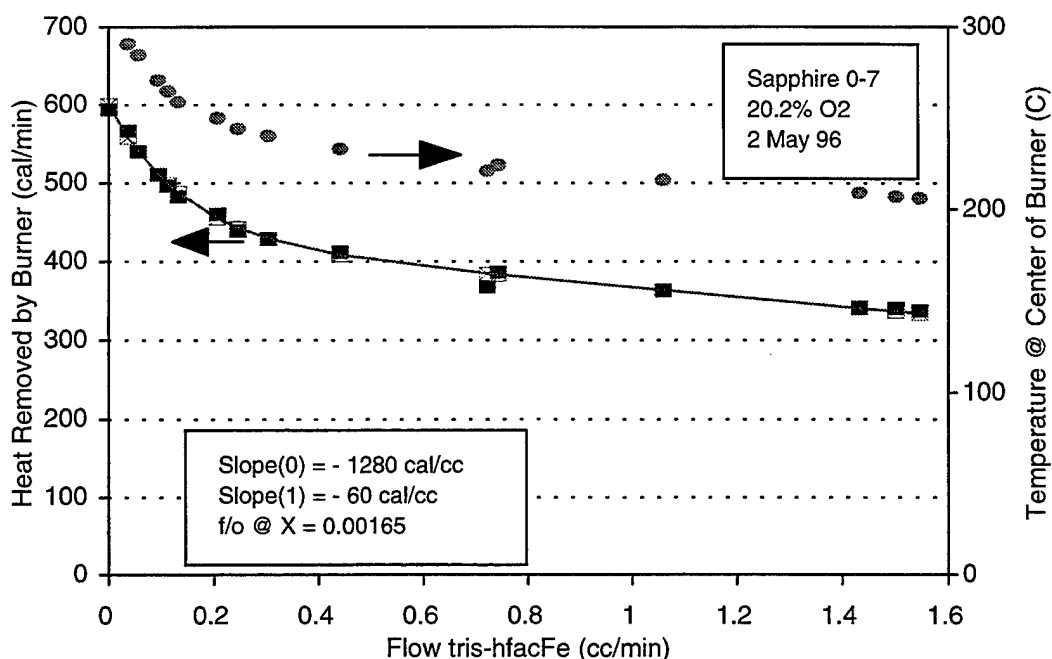
Figure 19. Tris-Hexafluoroacetylacetonatoiron(III) in a Methane-Air Flame with $\phi = 1.02$.

required to give the higher flow rates of Fe(hfac)$_3$. The inability to date to take the experiment to extinguishment does not appear to be due to some limitation of the chemistry, as the HRBB curve is still tending down at the end of the experiments (Figure 19).

5.   FeO Particle Size Measurements with the Fraunhofer Diffraction Photometer

The results of preliminary experiments with the Fraunhofer Diffraction Photometer are shown in Figure 20. These experiments validated the use of the Fraunhofer instrument in the active flame environment. The apparent bimodal distribution of particles (with maxima at 2 and 6 microns) remains to be confirmed with additional experiments.

From visual observations, it seems that the appearance of the luminous particles coincides with the point on the extinguishment curve (such as that displayed in Figure 19) at which the shape changes from exponential to linear. The Fraunhofer instrument will aid in verifying this qualitative observation.

57
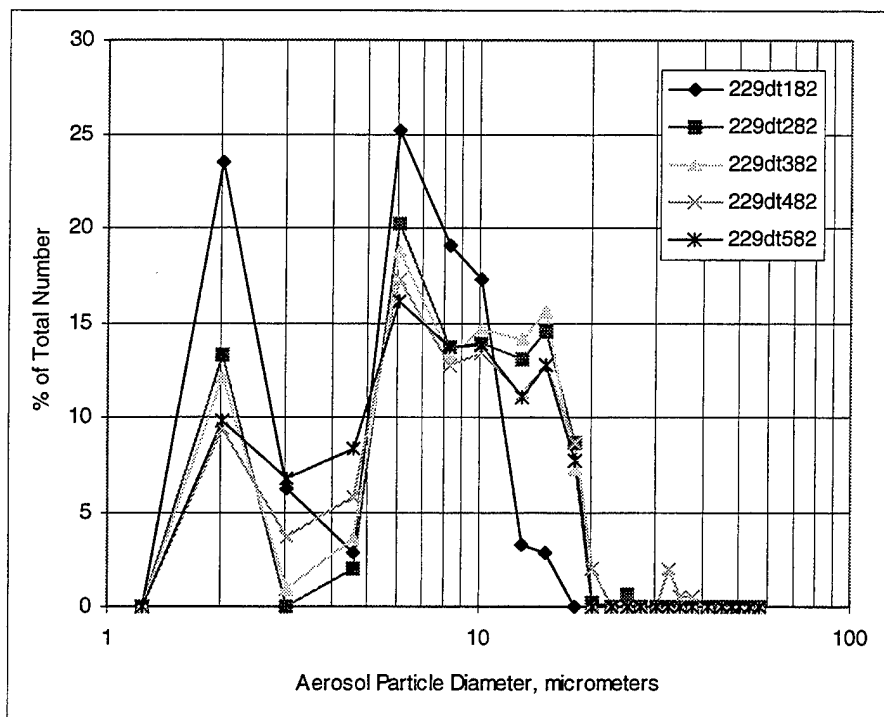
Figure 20. FeO Aerosol Particle Distribution by Diameter

6.   Emission Spectroscopy of Iron-Containing Flames

The emission spectroscopy of flames into which iron was introduced demonstrated a distinct change in the character of the flame as a function of the amount of iron added. As a point of reference, the reader is referred to Figure 12 or Figure 19. For very small amounts of added iron (less than 0.2 cc Fe(hfac)$_3$/min in Figure 19), the flame was observed to be orange and the spectrum was dominated by emission by the FeO molecule (Figure 21) (Reference 66). As the amount of iron was increased, luminous particles begin to appear in the flame and the spectrum began to be dominated by the broad feature illustrated in Figure 22. With relatively large amounts of added iron, the spectrum was entirely dominated by the broad emission, though the absolute intensity of the FeO emission appeared to remain constant. This broad, intense emission is assigned to chemiluminescence of a species closely related to the FeO molecule. This assignment is based on the following observations: (1) The feature is structured, having three principal maxima and two lesser peaks at shorter wavelengths. The three major peaks lie slightly to the red (at longer wavelengths) of the well-known FeO emission bands
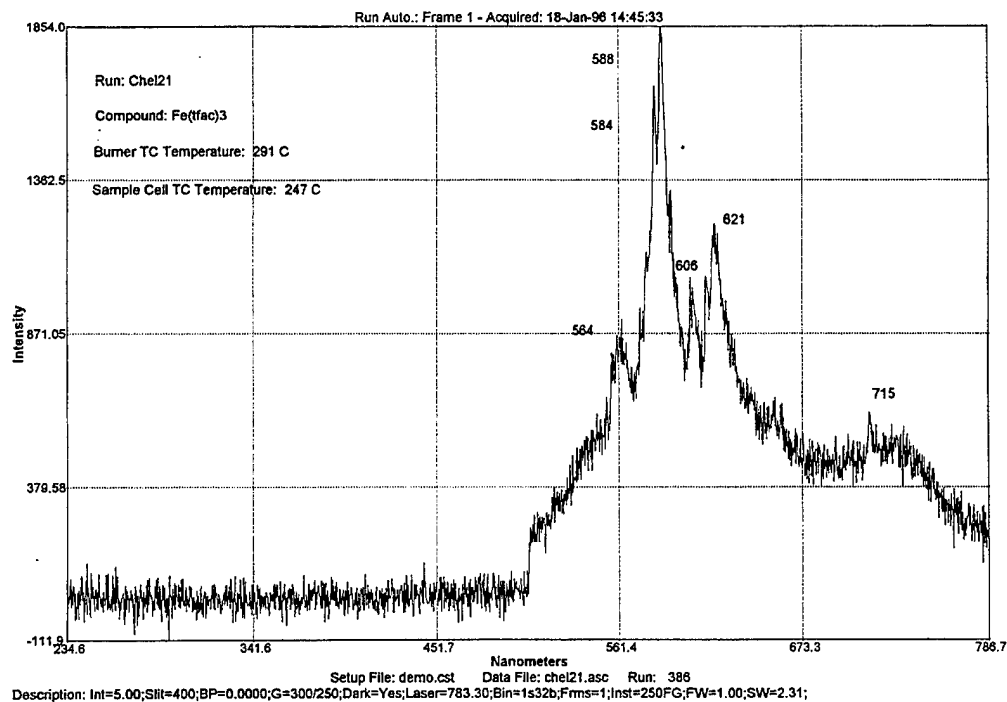
Figure 21. Emission Spectrum of FeO.
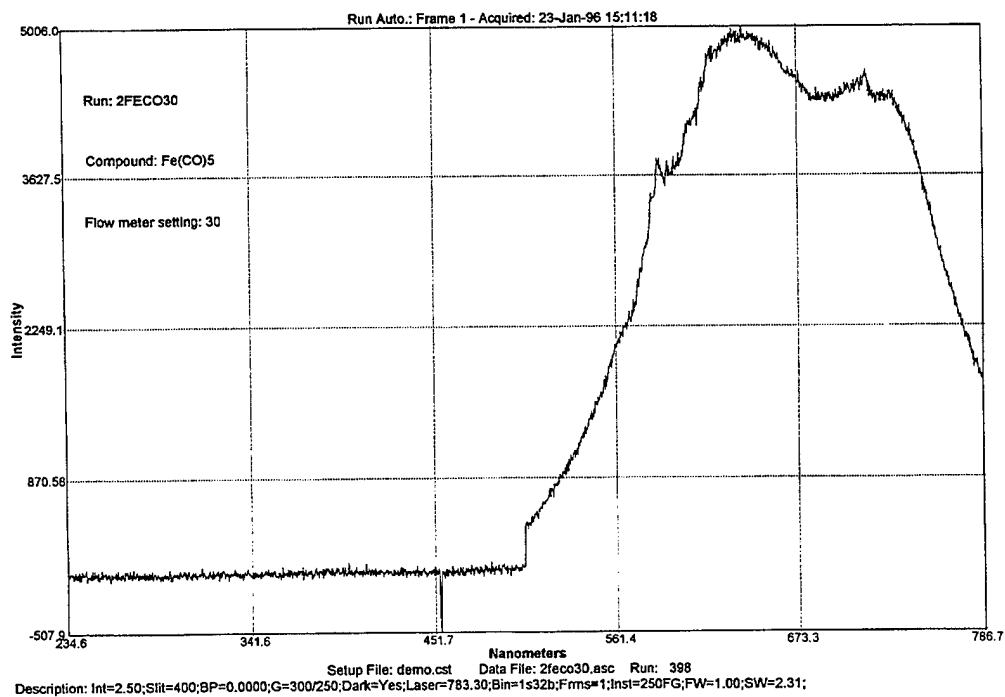
Figure 22. Emission Spectrum at High Concentrations of Fe(CO)₅.

59

and the two lesser peaks lie to the red of a more poorly characterized band system also thought to be attributable to FeO (Reference 62). (2) The broad feature clearly is not black-body radiation, which would not be structured, and would have a maximum at a wavelength longer than 1000 nm for flame temperatures typical of those in these experiments.

7.   Laboratory Streaming Experimental Results

Limited testing was performed with Fe(acac)$_3$ and Fe(hfac)$_3$. The Fe(acac)$_3$ was found to be insoluble in FC-5-1-14, and only slightly soluble in HFE-449s1, yielding a blend of 99.8 wt.% HFE-449s1 and 0.2 wt.% Fe(acac)$_3$. At a flow rate of 4.8 g/s, the extinguishment time was 9.8 seconds (close to that for pure HFE-449s1), and showed no improvement over pure HFE-449s1 performance. Experimental data for pure FC-5-1-14 and HFE-449s1 are displayed in Figure 23.
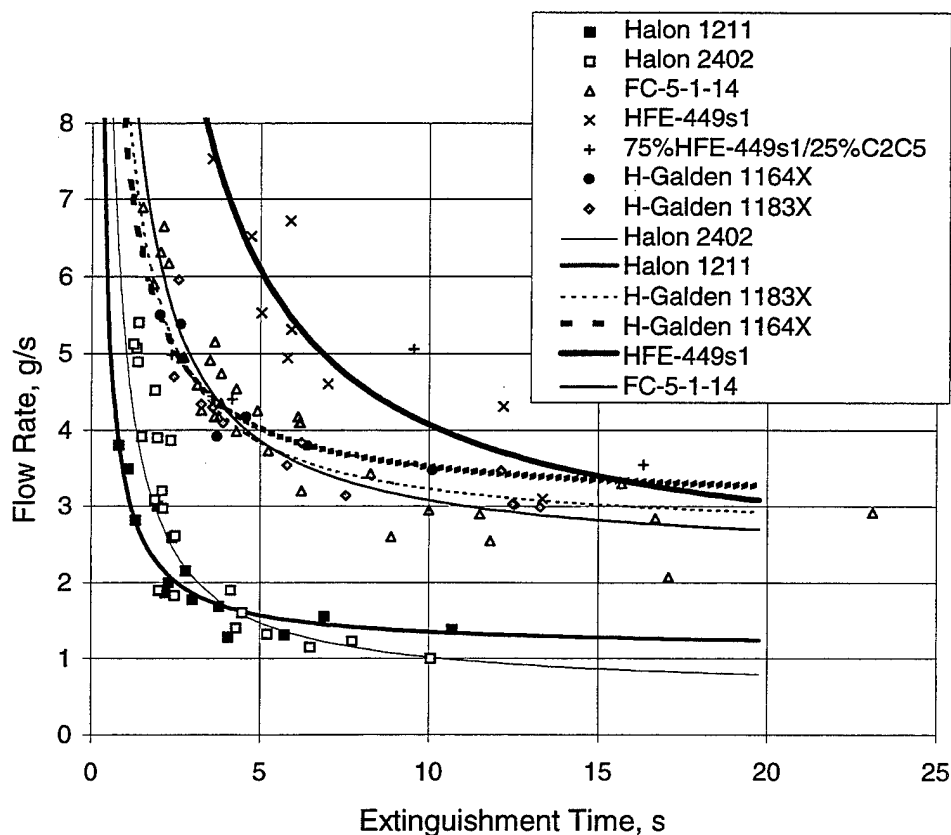
Figure 23. Results of Laboratory Streaming Experiments for Pure Agents.

The Fe(hfac)$_3$ was only partially soluble in FC-5-1-14 and was not tested with HFE-449s1 due to its unavailability at the time of the testing. The blend tested was 99.6 wt.% FC-5-1-14 and 0.4 wt.% Fe(hfac)$_3$, and again showed no improvement in performance over neat FC-5-1-14. At a flow rate of 4.3 g/s, the extinguishment time was 6.1 seconds.

Since the iron complexes are more soluble in methanol, an approximately 75 wt.% methanol and 25 wt.% Fe(hfac)$_3$ solution was prepared and tested. The Fe(hfac)$_3$ had not been recrystallized and some unreacted Fe(OH)$_3$ was present. The solution was ineffective; the fire could not be driven off the front of the pan, and it appeared that the agent blend made the fire larger. This result was very much unexpected. Many much less effective agents are available, which have "fuel character" and yet extinguish fires, e.g., HCF$_3$. In light of the extremely promising results obtained for Fe(hfac)$_3$ with the Sapphire burners, a hard look must be taken at these preliminary streaming results. Given the very limited solubility of the Fe(hfac)$_3$ in HFE-449s1 and FC-5-1-14, it is not particularly surprising that there was no apparent improvement in the extinguishing effectiveness of the blends compared with the neat solvents. The performance of the methanol blend is somewhat more surprising. The interpretation is no doubt complicated by the inherent flammability of methanol, and by the fact that Fe(hfac)$_3$ is not especially soluble in this solvent either (although the solubility in methanol *is* greater than that in either of the two fluorocarbon solvents). However, there may be a much more important issue at hand. In all the Sapphire burner experiments, the iron complexes were introduced as molecular species; in the streaming tests, the blends were introduced as droplets. It is very likely that the rate at which molecular Fe(hfac)$_3$ was released from the droplets was so slow that useful concentrations of the compound were not generated. Clearly, there is a critical need for an understanding of the particle parameters of an effective delivery system for this compound.

D.   DISCUSSION

From the results of prior work and of this investigation, it is clear that iron compounds catalytically inhibit flames, and that the important catalytic species involves the iron atom. The collective data are consistent with the following proposed description of the extinguishment by

61

these agents. At low concentrations of agent, the FeO molecule is the primary species and is engaged in homogeneous reactions.

At higher concentrations, the FeO molecules agglomerate to form FeO aerosols, possibly in concert with amorphous carbon (soot precursors) in the form of FeO seeded particles. It appears that the inhibition chemistry still involves the FeO molecule; however, the FeO molecule is perturbed by the environment in the aerosol particle, and the spectrum is shifted in the (expected) direction of longer wavelengths. Moreover, since many of the FeO molecules are now trapped in internal sites in the aerosol particles, relatively few are available on the surface of the particles to contribute to the inhibition of the flame.

Although this description is consistent with all observations to date, other possibilities cannot yet be ruled out conclusively, and several additional questions are of great interest. The answers to these and related questions are the objectives of continuing investigations in the NMERI laboratories.

(1) Does the Fe atom have a role in the catalytic mechanism?

(2) Is the fact that iron has several possible oxidation states, two of which (2+ and 3+) are very easily accessible, important? Experiments with metals having only one easily accessible oxidation state should provide insight into this question.

(3) Since the aggregation of the FeO molecules is clearly associated with reduced effectiveness, it may be asked whether there is some technique by which aggregation may be reduced or delayed. Does the onset and/or degree of aggregation depend on the nature of the agent?

(4) Another source of iron in flames is an aqueous aerosol containing $Fe(NO_3)_3$. Preliminary experiments with aerosols have demonstrated that FeO is generated in the flame, just as it is when $Fe(CO)_5$ and $Fe(hfac)_3$ are introduced into the flame (Reference 62). Can the $Fe(NO_3)_3$ aerosol lead to an effective extinguishing system?

(5) Do metals other than iron, such as manganese or titanium, have similar catalytic inhibition mechanisms?

(6) If it is necessary that the iron-containing agent be introduced as individual molecules, are there practical techniques for achieving this end?

SECTION IV

TOXICITY

A.   OVERVIEW

A detailed review of toxicity parameters is given in Volume IV of this series of reports
(Reference 67). Much of the toxicology and safety information presented in this report was taken
from Sax and Lewis and from the National Institute for Occupational Safety and Health (NIOSH)
Registry of Toxic Effects of Chemical Substances (References 68 and 69). The SAX Hazard
Rating (HR) has been given for some compounds. This rating indicates the relative hazard for
toxicity, fire, and reactivity with 3 denoting the worst hazard level. It should be noted, however,
that careful consideration of the actual threat may indicate that a lower rating may be more
appropriate for some compounds. For example, in some cases only toxicity by intraperitoneal,
subcutaneous, and/or intravenous routes (only indirectly related to toxicities of interest here) is
known. Moreover, emission of toxic combustion products such as HBr (emitted by all or nearly
all bromine-containing compounds including the present halons) appears to have been given
undue weight. An excellent example is the high HR = 3 given to ferrocene, bis(cyclopenta-
dienyl)iron(II), a compound considered by most to represent a very low hazard. Even tumorigen
and related warnings may be misleading. For example, ferrous gluconate is stated to be an
experimental tumorigen and teratogen even though it is widely used as a human dietary
supplement (Reference 69). Thus, toxicological evaluations must be carefully considered before
reaching any conclusions.

B.   METALS

The metals being considered as firefighting agents include cobalt, iron, manganese,
nickel, titanium, and zinc. In considering the toxic properties of metals, it is important to call
attention to certain general properties of this class of chemicals. Metals seldom interface with
biological systems in their elemental form. Rather, they occur as distinct compounds that vary
considerably in their ability to pass across biological membranes and hence, potentially cause

damage. Table 4 presents a classification of the effects and concerns surrounding metals (Reference 70). The metal complex is crucial for determining the specific toxicity of metal compounds. Table 5 shows several generalizations about the target organs for various types of metal compounds (Reference 70).

Soluble salts of metals dissociate readily in the aqueous environment of biological systems, thereby facilitating their transport as metal ions. On the other hand, insoluble metal salts are relatively poorly absorbed in the body, especially if they are in a polymeric state of aggregation. Even in the case of soluble salts, several factors influence their absorptivity, e.g., transport of soluble salts into biological systems may be hampered in the presence of anions that favor the formation of insoluble salts.

C.   LIGANDS

The toxicities (and properties) of free ligands are likely to be quite different from those of the complexed forms. The ligand may be in an entirely different physical state, and the free ligand could form a complex with essential metals in the body, where this could be impossible for the bound ligand. Moreover, the flammability information probably has little meaning. Nevertheless, there may be some information of importance. The data in Table 6 are taken from Reference 69.

D.   COMPOUNDS

Metal carbonyls are generally very hazardous, more so than the metal itself or other compounds (Table 4). For example, the acceptable level for metallic nickel and its soluble salts is 1.0 mg/m^3, whereas that for nickel carbonyl is 0.007 mg/m^3 (Reference 70). Metal hydrides and metal alkyls also tend to present a greater safety hazard (in both toxicity and reactivity) than other metallic compounds.

The route of entry plays an important role in determining the toxicity of a metal compound. Inhalation of metals may occur in firefighting scenarios. Solubility is particularly important in determining the fate of metals deposited in the respiratory airways. The more

TABLE 4. EFFECTS AND CONCERNS OF METALS.

Metal	Essential for mammals	Moderate to severe industrial hazard	Factors in environmental or nonoccupational disease	Accidental poison	Limited industrial hazard
Aluminum					+
Antimony		+		+	
Arsenic		+	+	+	
Barium					+
Bismuth					+
Boranes		+			
Chromium (III)	+				
Chromium (VI)		+			
Cobalt	+		+		
Copper	+			+	+
Gallium					+
Germanium					+
Iron	+		+	+	+
Lanthanides					+
Lead		+	+	+	
Magnesium	+				+
Manganese	+	+			
Metal hydrides and carbonyls		+			
Molybdenum	+				+
Nickel		+	+		
Strontium	+				+
Tin (organic)		+		+	
Titanium					+
Vanadium	+	+			
Zinc	+				+

TABLE 5. TARGET ORGANS OF METALS.

Metal	GI tract	Respiratory tract	CNS	CV system	Liver	Skin	Blood	Kidney	Bone	Endocrine
Aluminum		+								
Antimony	+	+		+	+	+				
Arsenic	+	+	+		+	+	+			+
Barium	+	+	+	+		+				
Bismuth					+	+		+		
Boranes		+			+			+		
Chromium		+	+		+	+		+		
Cobalt	+	+	+	+		+				+
Copper	+						+			
Gallium			+			+		+	+	
Germanium	+	+		+						
Iron	+	+	+		+		+			+
Lanthanides		+			+		+			
Lead	+		+				+	+		
Magnesium			+							
Manganese		+	+							
Metal hydrides							+			
Molybdenum					+		+	+	+	
Nickel		+	+			+				
Strontium				+						
Tin (organic)	+		+							
Titanium		+								
Vanadium		+	+			+		+		
Zinc	+						+		+	

66

TABLE 6. TOXICOLOGICAL AND SAFETY INFORMATION FOR LIGANDS.

Compound	Formula	CAS No.	Observations[a]
acetylacetone	$CH_3C(O)CH_2-C(O)CH_3$	123-54-6	[ABX750] LC_{LO} (rat, inhalation) = 1000 ppm, LD_{50} (rat, oral) = 1000 mg/kg, LD_{50} (rabbit, skin) = 5000 mg/kg. Moderately toxic by ingestion, intraperitoneal, inhalation. HR = 3.
12-crown-4	$C_8H_{16}O_4$	294-93-9	[COD475] TC_{LO} (rat, inhalation, 7 hr) = 1, 0.5 ppm, LD_{50} (rat, oral) = 2830 mg/kg, LD_{50} (mouse, oral) = 3150 mg/kg. Moderately toxic by ingestion, intraperitoneal routes. Eye, skin irritant. HR = 2.
18-crown-6	$C_{12}H_{24}O_6$	17455-13-9	[COD500] LD_{50} (rat, oral) = 1390 mg/kg, LD_{50} (mouse, oral) = 705 mg/kg. Moderately toxic by ingestion, intraperitoneal. Eye, skin irritant. HR = 2.
dibenzo-18-crown-6	$C_{20}H_{24}O_6$	14187-32-7	[COD575] LD_{50} (rat, oral) = 2600 mg/kg. Moderately toxic by ingestion, intraperitoneal. Eye, skin irritant. HR = 2.
1,3-cyclopentadiene	$-CH=CH-CH=CH_2CH_3-$	542-92-7	[CPU500] Little toxicity information. Probably moderately toxic by inhalation. Dangerous fire hazard. HR = 3.
dicyclohexyl-24-crown-8	$C_{24}H_{44}O_8$	17455-23-1	[DGT300] LD_{50} (rat, oral) = 75 mg/kg. Poison by ingestion, intraperitoneal. Eye, skin irritant. HR = 3.
dicyclohexyl-18-crown-6	$C_{20}H_{36}O_6$		[DGV100] LD_{50} (rat, oral) = 176 mg/kg, LD_{LO} (rat, skin) = 130 mg/kg. Poison by ingestion, skin contact, intraperitoneal. Eye, skin irritant. HR = 3.

[a]The SAX Number (Reference 69) is given in brackets followed by information from that reference. "HR" denotes the SAX Hazard Rating.

insoluble the metal compound, the more likely it is to be cleared from the pulmonary tract by retrograde movement to the pharynx and then swallowed. With retrograde movement, systemic absorption is minimized.

Lung levels of certain metals such as titanium, chromium, tin, cadmium, lead, and aluminum increase up to age 40 years due to the accumulation of insoluble particles. Levels of nickel, tin, strontium, cadmium, and lead increase in other tissues as well due to inhalation and then relocation within the body (Reference 70).

Topical exposure to certain metals may also present a hazard in firefighting settings resulting in skin and eye irritation or sensitization and also providing an avenue for absorption causing systemic toxicity. Dermal exposure to abraded skin can produce serious toxicity concerns. Cobalt and nickel are the only metals being presently considered that have the skin as a target organ.

Careful consideration of all transition metals indicates that iron and manganese are the most promising candidates. Titanium also has a low toxicity; however, multiple oxidation states (if this is important) are not as readily achieved. Although some of the noble metals, such as gold and platinum, may have relatively low toxicities (depending on the route of introduction and the compounds); the expense of these materials appears to rule them out. Note, however, that it could be possible to use these materials in very specialized forms without undue expense (e.g., monolayers on substrates, cluster compounds if highly effective, etc.). The rare earths are another possibility; however, there are little toxicity data available on toxicity by inhalation, the most probably route for introduction during use as extinguishing agents.

A large number of iron salts are assigned HR = 3, a rating based almost solely or ingestion (Reference 69). In general, ferrous (iron(II)) compounds are more toxic than ferric (iron(III)) compounds.

Manganese and its compounds are on the EPA Community Right-To-Know List. Fumes and dust of manganese compounds can cause central nervous system (CNS) and pulmonary system damage, and chronic poisoning is possible for exposures over several months or longer.

When well established, chronic manganese poisoning causes a permanent disability. Few poisonings have occurred from ingestion.

Table 7 gives some information on toxicity and safety of metal compounds related to those of interest (Reference 69). Methylcyclopentadienyl-tricarbonylmanganese(I) has been used as an antiknock agent for gasoline.

TABLE 7. TOXICOLOGICAL AND SAFETY INFORMATION FOR METAL COMPOUNDS.

Compound	Formula	CAS No.	Observations[a]
bicyclopentadienylbis-(tricarbonyl)iron(I)	$(CO)_3Fe(C_5H_4-C_5H_4)Fe(CO)_3$		[BGA500] LD_{50} (rat, oral) = 2900 mg/kg. Moderately toxic by ingestion, intraperitoneal.
bis(benzene)iron(0)	$Fe(C_6H_6)_2$		[BGZ000] Explosive gas that can detonate at -40 °C.
cyclopentadienyl-tricarbonyl-manganese(I)	$Mn(C_5H_5)(CO)_3$		[BGA500] LC_{LO} (rat, inhalation, 2 hr) = 120 mg/m^3, LD_{LO} (rat, oral) = 20 mg/kg. Moderately toxic by ingestion, intraperitoneal.
bis(cyclopentadienyl)-iron(II), ("ferrocene")	$Fe(C_5H_5)_2$	103-54-5	[FBC000] LD_{50} (rat, oral) = 1320 mg/kg, LD_{50} (mouse, oral) = 832 mg/kg. Poison by intraperitoneal, intravenous. Moderately toxic by ingestion. Experimental tumorigen. Suspected carcinogen. Flammable. HR = 3.
tris(acetylacetonato)-iron(III)	$Fe[CH_3C(O)-CHC(O)CH_3)]_3$	14024-18-1	[IGL000] Poison by intravenous route. HR = 3.
manganese(II) acetate	$Mn(OOCCH_2)_2$	638-38-0	[MAQ000] LD_{50} (rat, oral) = 2940 mg/kg. Moderately toxic by ingestion. HR = 2.
bis(acetylacetonato)-manganese(III)	$Mn[CH_3C(O)-CHC(O)CH_3)]_2$	14024-58-9	[MAQ500] Experimental neoplastigen and tumorigen. HR = 3.
methylcyclopentadienyl-tricarbonyl-manganese(I)	$Mn(C_5H_5CH_3)(CO)_3$		[MAV750] LC_{50} (rat, inhalation, 7 hr) = 76 mg/m^3, LC_{50} (mouse, inhalation, 4 hr) = 58,600 μg/m^3, LD_{50} (rat, oral) = 50 mg/kg. Poison by ingestion, inhalation, skin contact, intravenous, intraperitoneal. HR = 3

[a]The SAX Number (Reference 69) is given in brackets followed by information from that reference. "HR" denotes the SAX Hazard Rating.

SECTION V

ADDITIONAL INFORMATION ON METAL COMPOUNDS

A.   IRON COMPOUNDS

1.   Tris(acetylacetonato)iron(III) – Fe(acac)$_3$

a)   Properties

M.p.: 178-183 °C (352-361 °F)

Physical color: red crystals

Molar heat of sublimation: 4.67 kcal

Sublimation temperature: 69 °C (156 °F)

Solubility: see Table 8

TABLE 8. TRIS(ACETYLACETONATO)IRON(III) SOLUBILITY IN VARIOUS ORGANIC SOLVENTS WITH TEMPERATURE.

Solvent	Temperature, °C	Fe(acac)$_3$, g/100g solvent
Benzene	20	52.0
	30	57.7
	40	66.0
Toluene	20	21.5
	30	26.0
	40	29.0
Acetylacetone	20	12.7
	30	18.1
	40	17.7
Methylcyclohexane	30	0.27
n-Heptane	20	0.11
	30	0.10
	40	0.21

b)   Decomposition and decomposition products

Reference 71 outlines the results for Fe(acac)$_3$ samples heated for 1 to 50 hours at 191 °C (376 °F) under an inert (nitrogen) atmosphere. The results showed the trivalent Fe chelate to be quite unstable yielding volatile products equivalent to 1.27 - 1.47 moles for each mole taken. Reference 72 carried this study further, the thermal stabilities of 9 metal chelates, over a temperature range of 150 - 400 °C (302-752 °F) in the absence of oxygen, was studied. Fe(acac)$_3$ decomposition temperature was found to nearly coincide with its melting point. Decomposition products were predominantly acetone and carbon dioxide. The order of decreasing heat stability for the acetylacetonates, based on the evolution of gaseous products, was found to be Na(I) > Cr(III) > Al(III) > Ni(II) > Cu(II) > Fe(III) > Co(II) > Co(III) > Mn(III).

Reference 73 reports on autoxidation experiments carried out at 98.5 °C (209 °F) under pure oxygen at atmospheric pressure in diphenyl ether as the solvent. The main autoxidation products of Fe(acac)$_3$ were carbon dioxide, water, biacetyl, acetic acid, acetylacetonate, mesityl oxide and an amorphous iron residue approximating the formula FeC$_7$H$_8$O$_{4.85}$. From material balances, the combined oxygen content of the products showed 3.86 moles of oxygen absorbed per mole of Fe(acac)$_3$.

c)   IR Spectra

Reference 74 listed the infra-red (IR) spectra from 4000 to 400 cm^{-1} for the Co(III), Cr(III), Fe(III), and Al(III) acetylacetonates. Reference 75 reported the IR spectra of Cr(III), Fe(III), Al(III), and Mn(III) acetylacetonates to 400 cm^{-1}.

d)   Synthesis

The literature gives a multitude of methods for the synthesis of Fe(acac)$_3$, several of which are discussed below.

The synthesis of the Fe(acac)$_3$ used in this program followed the method outlined by Chaudhuri and has already been described (Reference 61).

Reference 76 listed the following methods for synthesizing Fe(acac)$_3$.

(1) The direct reaction of the 1,3-diketone with metals salts in an aqueous solution. This reaction will come to equilibrium short of completion because of the increase in concentration of free acid in the solution. The easiest ways to overcome the free acid is to control the pH by buffering the solution. Use of metal acetates for pH control by gradually adding a base, preferably ammonia or urea, are among the most common methods. Solubility problems can be overcome, in part, by using a slightly polar nonaqueous solvent (a mixture of water and ethanol or dioxane) or by adding the 1,3-diketone in ethanolic (or similar) solution to the aqueous solution of the metal salt. The metal complex then needs to be filtered from the water or the nonaqueous solution must be evaporated to obtain the metal complex. (2) In nonaqueous solutions where both the metal halide and the 1,3-diketone are soluble in an inactive organic solvent such as benzene, the reaction can be brought to completion by warming, since the hydrogen halide formed is insoluble in the reaction medium. (3) Incorporation of solvent extraction with method 1 or 2. This uses the above methods to produce the 1,3-diketone compound, then removes the compound as it is formed. Since metal hydroxides and such species as MChX, MChOH, MCh$_3^-$ (where Ch = 1,3-diketone ligand) are seldom soluble in an organic medium, the extraction liquid separates the desired compound from these contaminants and can be recycled through the system repeatedly.

Reference 71 prepared the Fe(acac)$_3$ by dissolving 67.6 g (0.25 mol) FeCl$_3$•6H$_2$O in 250 mL of water, which was then added to 50 g of acetylacetone (0.5 mol) in 100 mL of methanol, while stirring. To the resulting mixture, a solution of 0.5 mol of sodium acetate in 150 mL of water was added. The mixture was heated briefly, cooled to room temperature, and refrigerated for several hours. The resultant crystals were filtered with a Buchner funnel, washed with water and dried in a vacuum desiccator. Recrystallization was carried out using a methanol-water blend. This procedure yielded a 99 percent conversion and recovery for the Fe(acac)$_3$.

Reference 77 used the following general method for preparation of a series of metal chelates. The nitrate salt of the metal was made up as a 5 wt.% solution and buffered immediately before use by adding 5 g of sodium acetate for every 100 mL of solution. The buffered metal ion solution was shaken with an alcoholic solution of the ligand until the reaction

appeared complete. After precipitation the chelate was collected by filtration and recrystallized by subliming at 80 °C and 0.2 mm of mercury.

And finally, Reference 78 reacted acetylacetone and iron carbonyl ($Fe(CO)_5$) under nitrogen at 135 °C (176 °F), shielded from light. The excess acetylacetone was removed and the solid recrystallized from an acetone solution by addition of water. A second recrystallization was carried out by adding n-heptane to a benzene solution.

2.   Tris(trifluoroacetylacetonato)iron(III) - Fe(tfac)$_3$

a)   Properties

M.p.: 114-115 °C (237-239 °F)

Physical color: red crystals

Molar heat of sublimation: 20.8 kcal

Sublimation temperature: 48 °C (118 °F)

b)   Synthesis

The synthesis of the Fe(tfac)$_3$ used in this program followed the method outlined by Chaudhuri except that 1,1,1-trifluoro-2,4-pentanedione was substituted for acetylacetone on a per mole basis (Reference 61). All other preparation steps were the same. Some additional synthesis methods outlined in the literature are discussed below.

The synthesis of Fe(tfac)$_3$ used in Reference 77 followed the same method of preparation except that recrystallization was from petroleum ether and the crystals were dried at 50 °C (122 °F) and at 0.5 mm of mercury.

Reference 79 reports a preparation method in which an aqueous solution (100 mL) containing 2.7 g (0.010 mol) iron(III) chloride hexahydrate and 5.0 g sodium acetate was shaken with an ethanolic solution containing 7.4 g (0.048 mol) 1,1,1-trifluoro-2,4-pentanedione. After approximately 10 min, the red crystalline solid that had precipitated was collected, washed with water, and air dried. The yield was 54 percent.

Additionally, Reference 80 outlined a preparation method where an aqueous solution of trifluoroacetylacetonates was neutralized with ammonium hydroxide and then added to an aqueous solution of the metal ion. The product was separated by filtration or extraction and purified by recrystallization and, in some instances, by sublimation at reduced pressure.

3.   Tris(hexafluoroacetylacetonato)iron(III) - Fe(hfac)$_3$

a)   Properties

M.p.: 47-49 °C (116-120 °F)

Physical color: red crystals

b)   Synthesis

The synthesis of the Fe(hfac)$_3$ again used the method outlined by Chaudhuri except that 1,1,1,5,5,5-hexafluoro-2,4-pentandione was substituted for acetylacetone on a per mole basis (Reference 61). All other preparation parameters were the same.

Additional synthesis methods would encompass the methods discussed above with the only change being the reagent substituted on a per mole basis.

SECTION VI

ASSESSMENT

Although the original motivation for experimenting with metal-containing compounds (such as $NaHCO_3$) was the thought that these compounds could be useful vehicles for introducing CO_2 at the sources of fires, it was quickly discovered that these compounds were unexpectedly effective extinguishing agents, and it was suspected that the metal was playing an important role in the extinguishment process. Today, dry chemical fire extinguishing systems are well established. Moreover, due in large part to the success of these metal-containing compounds, considerable effort has been devoted both to an investigation of the mechanisms by which metals are involved in flame chemistry, and to a search for even more effective metal-containing compounds. To date, the fire suppression/inhibition properties of well over 100 metal-containing compounds, involving 33 or more different metals, have been studied.

It is now well established that both physical and chemical processes contribute to the extinguishing effectiveness observed for metal-containing compounds. Physical, or thermal, mechanisms are characteristic of all compounds; all compounds absorb energy from high temperature environments by virtue of their intrinsic heat capacities, and many absorb additional energy through phase transitions (such as vaporization) and/or transformations (such as decomposition).

At the same time, it is also well established that many metals and/or their compounds catalyze the recombination of flame radicals (especially H atoms and $\bullet OH$ radicals), thereby upsetting the flame chemistry and contributing to extinguishment.

It has been shown that the extinguishing effectiveness of many metal-containing compounds can be correlated quantitatively with their thermal mechanisms and that, even though catalytic processes may also be operative, it is unnecessary to invoke these catalytic processes to account quantitatively for the effectiveness of these compounds. The metals for which this is true include both the alkali (Group IA) and alkaline earth (Group IIA) metals.

75

At the same time, metal-containing compounds are so effective (especially when only very small amounts of the compounds have been introduced into the flame) that their behavior cannot be accounted for in terms of thermal mechanisms alone. It is this subset of extraordinarily effective metal-containing compounds that appears to offer potential for next-generation extinguishing agents. Perhaps the most thoroughly studied compounds in this subset are tetraethyl lead and iron pentacarbonyl. The former has been studied principally in relation to its influence on preignition knock in internal combustion engines, while the latter has been studied mainly from the vantage point of its flame extinguishing properties.

From extensive work with $Fe(CO)_5$ in our own laboratories (sponsored in part by AFOSR), there is no question that introduction of $Fe(CO)_5$ leads to the catalytic extinguishment of the flame. The initial part of the experimental curve (of heat removed by the burner (HRBB) vs amount of $Fe(CO)_5$ added) shows an exponential decrease in extinguishing effectiveness as a function of amount of $Fe(CO)_5$ added. This is precisely the same sort of behavior exhibited by Halon 1301, which is well known to extinguish the flame by a mechanism involving catalytic recombination of H atoms. The reason for the exponential decay is not certain at the moment, but two hypotheses are being considered.

(1) On the one hand, it may be that the first few molecules of extinguishing agent find a "target rich" environment, with many candidate flame radicals (H atoms, •OH radicals, and perhaps also O atoms). The first few molecules of extinguishing agent are extremely effective in catalyzing the recombination of these flame radicals. However, as more and more agent is added, the number of available flame radicals is fewer and fewer, and the effectiveness falls off simply because of the increase in the mean time between collision of an extinguishing molecule with a flame radical.

(2) On the other hand, the exponential fall off may reflect the fact that the recombination of two flame radicals (e.g., H + H and/or H + OH) is very exothermic, and locally increases the available energy in the flame. This increased available energy increases the fraction of the remaining H atoms, which have sufficient energy to overcome the activation energy barrier of the flame initiation reaction(s). Thus, the removal of some of the flame radicals results in an *increase* in the kinetic energy of the

76

remaining radicals, making them *more* effective in initiation and propagation reactions. As a consequence, the observed degree of inhibition is less than one would have anticipated based strictly on the number of flame radicals removed by the extinguishing agent.

Of these two hypotheses, the latter is gaining credence over the former, and leads to the following further considerations. As a starting point, it is noted that the overall extinguishing effectiveness of $Fe(CO)_5$ is greater than can be accounted for strictly by thermal mechanisms, but less than that expected from a catalytic mechanism (as evidenced by the initial slope of the HRBB curve). This suggests that the limiting characteristic is still the rate at which heat can be removed from the flame. There is some important evidence bearing on this point. For one thing, it is known that methane-air flames are extinguished more effectively by $Fe(CO)_5$ than methane-oxygen flames. This observation is consistent with the hypothesis that the added diluent (nitrogen) in the methane-air flame is facilitating dispersal of the energy released by the catalytic recombination step. In addition, it is known that $Fe(CO)_5$ is more efficient at atmospheric pressure than in reduced pressure flames, which is consistent with this hypothesis.

In view of the available evidence, it appears that, when the catalytic mode is operative, there may be an additional channel for heat removal. With the exception of diluents in the flame, there are not many candidates. The most obvious candidate is heat removal by visible radiation. For flames doped with very small amounts of $Fe(CO)_5$, the FeO emission is prominent, while for more heavily doped flames, chemiluminescence originating (presumably from FeO molecules) on the surfaces of the particulates in the flame is very intense. Needless to say, to account for the total amount of heat removed from the flame solely by radiative mechanisms would imply a much brighter flame than is actually observed. However, when one examines the number density of H atoms entering the pre-flame region, the number of H atoms that must be removed from the flame is relatively small. An important question here then becomes: Is there any propensity for catalytic recombination of "hot" H atoms? The answer is most likely "no," given the lack of activation energies for typical free radical reactions. Of course, not all the H atoms must be removed; below some threshold critical density, extinguishment will be encountered.

The specific species involved in the extinguishment also remains uncertain at the present time. The most that can be said is that an iron-containing decomposition product of $Fe(CO)_5$ is the catalytically active species. The observed FeO and perturbed FeO chemiluminescent emissions implicate the FeO molecule. While the FeO molecule could be the key to the catalytic cycle, it might simply be the species in which the energy is pooled for subsequent radiation. In this regard, it is important to note that $Fe(CO)_5$ is a relatively poor extinguishant in fuel-lean flames, while being more than twice as effective in fuel-rich flames. The two working hypotheses at the moment are these.

(1) The FeO (or some other relatively simple molecular species involving iron) generated in the flame catalyzes the oxidation of CO in fuel-lean flames. This reaction would result in additional heat released in these flames, making the $Fe(CO)_5$ a less effective agent for flames of this composition.

(2) The catalytically active species may be suppressed in lean flames. It is noted especially that fuel-rich flames are reducing flames (having higher H atom concentrations) and tend to shift equilibria away from metal oxides and toward metal atoms.

While the majority of the data accumulated to date has been acquired for the $Fe(CO)_5$ system, important information has been obtained with the hexafluoroacetyl-acetonatoiron(III), $Fe(hfac)_3$, system. Perhaps most important of all, the HRBB experiments have shown that the behavior of $Fe(hfac)_3$ directly parallels that of $Fe(CO)_5$. Thus it can be said conclusively that the important mechanism is catalytic, and that the catalytically active species is the same for both agents. It is also true that any limitations of the $Fe(CO)_5$ system (excluding concerns about toxicity) are probably shared by $Fe(hfac)_3$. There may be one exception to this statement: It is not known at this point how the extinguishing effectiveness of $Fe(fhac)_3$ compares in fuel-lean flames with that in fuel-rich flames. While there is no particular reason to expect that the behavior of $Fe(hfac)_3$ should be different from that of $Fe(CO)_5$, allowance must be made for this possibility. Experiments to clarify this point are scheduled.

To this point in the discussion, virtually all of the emphasis has been placed on the understanding of the processes at the microscopic (molecular level). If there were a single comment to sum the information to this point, it might be the following: The extinguishment of flames by iron-containing compounds involves a very sensitive balance of several heat-releasing and heat-absorbing processes. Moreover, the order in which the various reactions happen in the flame is doubtless of vital importance. While iron is probably not unique with respect to the ability to strike the appropriate balance, the unusual effectiveness of iron compounds may well be the result of this unique balance. At the same time, it would be a grave error to ignore the macroscopic events that also accompany the flame suppression processes. Of particular importance is the role of the particulates formed at large iron concentrations. Unfortunately, more questions than answers arise at this point. Some of the key questions are listed below, and the answers to these questions may do more to determine the ultimate value of iron compounds than all the information concerning the microscopic details.

(1) If (as seems probable, based on the experimental observations) the mechanism changes from a homogeneous catalytic recombination mechanism to a heterogeneous catalytic recombination mechanism with the appearance of the particles, can the point of transition be altered?

(2) Does the starting material (i.e., the nature of the agent) have an influence on the onset of the formation of particles?

(3) Can aqueous aerosols (of $Fe(NO_3)_3$, for example) be as effective as the organometallic forms of iron?

(4) Can misting systems (either organometallic, in non-aqueous solvents, or iron salt, in aqueous systems) be used effectively to dispense and disperse the iron compounds?

(5) In an aerosol mist, do the "right" reactions occur in the "right" sequence to yield the catalytic iron species?

While nearly the entire discussion to this point has focused on iron-containing systems, this is largely because more is known about them. However, several other metals also have very promising extinguishing characteristics. Chromium must be mentioned briefly. Because of concerns with chromium in the environment, it is hard to imagine the use of this element in fire

extinguishment. However, the demonstrated effectiveness of chromium, for example, strongly suggests that iron is not unique in the Periodic Table. Indeed, several other metals (including manganese) have demonstrated attractive extinguishing properties; therefore, it is premature to settle on iron. Moreover, as more is learned about the specific details of the interactions of iron and other metals with flames, one may yet discover the fundamental property, or the key, to selecting a metal-containing compound for the next generation fire extinguishing agent.

What then should the next steps be? To begin with, it is essential to note that key scientific issues remain to be resolved; the understanding of extinguishment mechanisms at the microscopic (molecular level) is not yet complete. Nevertheless, in spite of a lack of complete understanding of these issues, it is apparent that metal-containing compounds have tremendous promise. Therefore, the principal issue at this point is the bridge between the microscopic behavior and the behavior in practical fire suppression scenarios. It is essential to discover whether the promise offered by the microscopic experiments can be realized in real-world situations.

For metal-based systems, the key difference between basic laboratory experiments and practical delivery systems appears to be this. In laboratory experiments conducted to date, the agent can be (and typically has been) dispersed at the molecular level. As a consequence, many of the issues associated with aerosols and particles have been largely ignored. (The exception is, of course, the attention given to the formation of luminous particles in the flames doped with relatively large amounts of iron compounds.) Some of the important questions that remain to be resolved are listed below. In reading this list, the reader is already aware that some of these questions are similar to those that have been investigated in the closely allied studies of dry chemical systems.

(1) How does the proposed heterogeneous extinguishment mechanism for metal-based systems compare with the homogeneous mechanism? Is it practical to consider a system in which both mechanisms are operative, or must one design the system so that the homogeneous (or, less likely, the heterogeneous mechanism) is dominant?

(2) Assuming that the metal-containing compound will be introduced as an aerosol, is there a critical maximum diameter above which the aerosol particle is not as effective? Is it essential to completely vaporize the particle to assure maximum effectiveness?

(3) Does the solvent system make a difference as to the size of the resultant aerosol particle? Does this system make a difference with respect to the ease or difficulty of interaction (vaporization, decomposition, etc.) of the particle with the flame?

(4) What is the optimum ligand, and what is the magnitude of its effect on the properties of the agent? How does the selection of the ligand affect the solubility, volatility, and reactivity of the metal-containing compound? To what degree does the ligand direct the initial decomposition chemistry of the metal containing compound? Does the ligand favor (or inhibit) production of the chemically-active species?

Fortunately, the gap between current laboratory experiments and the behavior in practical delivery systems can be bridged largely by straightforward extensions of current laboratory experiments. The behavior of aerosol particulates can be addressed by several different laboratory experiments (examples given below) in which the basic laboratory diagnostic tools are retained to decipher the microscopic behavior as the particulates interact with the flame environments.

(1) Study of aerosols in premixed flames. Both aqueous and non-aqueous aerosols should be investigated. Especially in the case of the aqueous aerosols, both dry and wet particles can and should be studied. Premixed flames have the advantages of simplicity, the ability to study degree of inhibition as a function of the amount of agent added, and the capability to investigate extinguishment effectiveness as a function of fuel-oxidizer equivalence ratio.

(2) Study of aerosols in counterflow diffusion flames. Studies in counterflow diffusion flames complement work in premixed flames. In particular, it is possible (in most cases) to study the effects of adding the agent both to the fuel stream and to the oxidizer stream.

(3) Study of aerosols in misting systems. In many respects, a misting system is a variant of a counterflow diffusion flame. The key difference is the role of convective flow in misting systems as compared with directed flow in conventional counterflow systems. A misting system is a step toward practical delivery systems; indeed, it has been shown that laboratory-scale misting systems are scalable (Reference 81).

The apparatus that makes possible the study of aerosols in premixed and counterflow diffusion flames is the modified Meker burner (such as the Sapphire burners developed and perfected in our laboratories). Burners of this type have grids (rather than frits) as flame holders, and may have as much as 64 percent open space through which the aerosols may be introduced with the flame gases.

The importance of using laboratory diagnostics to characterize the behavior of the flames can not be over emphasized. Non-intrusive probes such as ultraviolet, visible and infrared emission, and absorption spectroscopy yield a great deal of information as to the microscopic processes. In additional to the more traditional spectroscopic techniques, laser-induced fluorescence is a particularly useful tool, and the relatively new cavity ring-down laser technique offers the greater sensitivity needed for transient species. Additional non-intrusive techniques include aerosol particle size and distribution measurement by methods such as Fraunhofer scattering. These can be supplemented by intrusive measurement devices such as thermocouples, although there are non-intrusive techniques for measuring temperature as well.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

A.   CONCLUSIONS

(1) Metal-containing compounds are very effective fire extinguishing agents, and some are known to be more effective than Halon 1301, CF_3Br.

(2) Catalytic recombination of flame radicals is a general extinguishment mechanism for metal-containing compounds.

(3) The relative importance of the catalytic recombination mechanism vis-a-vis the physical (thermal) mechanism depends on several parameters including flame temperature and the fuel-oxidizer equivalence ratio.

(4) For Group IA (alkali) metals and Group IIA (alkaline earth) metals, the physical (thermal) mechanism predicts the extinguishment effectiveness even though the catalytic recombination mechanism may be at work concurrently.

(5) To account for the exceptional extinguishment effectiveness of many of the remaining metals in the periodic table (especially the transition metals, but not excluding the main group metals), it is necessary to invoke contributions due to the catalytic recombination of flame radicals in addition to the usual thermal mechanisms.

(6) There is not a complete understanding of the details of extinguishment by iron containing compounds, which are perhaps the most thoroughly studied of the metal containing compounds outside of the Group IA and Group IIA metals.

(7) Several metals, including iron and manganese, offer significant promise.

(8) The importance of delivery techniques (such as misting, dry aerosol generation, etc.) is recognized, but there is far too little information on the influence of the technique on the effectiveness of the agent.

(9) Metals themselves do not normally interfere with biological systems in their elemental form, and are considered fairly non-toxic. However, when they occur as compounds, they may pass biological membranes, and potentially cause damage.

83

Metal carbonyls present hazards greater than the metal itself or other compounds. The route of exposure is critical for metals used as fire extinguishing agents; however, little toxicity data are available on rare earths and other metals being considered. The toxicities and properties of free ligands are likely to be quite different from those of the complexed forms.

B.   RECOMMENDATIONS

(1) Metal compounds should be retained in the competition for next generation agent(s).

(2) Using iron compounds as a baseline, work should continue to elucidate the details of the extinguishing mechanism(s).

(3) Manganese should be selected as a second metal for study and the results from examination of this metal be compared and contrasted with the data for the iron compounds.

(4) Using iron compounds as a baseline, the effects of potential delivery techniques should be examined in premixed flames, counter-flow diffusion flames, and misting systems. As a minimum, the following techniques should be investigated: dry powder, aqueous aerosols (both with and without evaporation of the water), and non-aqueous mists.

(5) The toxicity of compounds proposed for future research should be investigated concurrently with any suppression research. This applies to both manganese and iron compounds, as well as others that may prove suitable for advanced testing.

APPENDIX A

SURVEY OF METAL COMPOUNDS TESTED FOR FIRE SUPPRESSION ACTIVITY.

Common and/or Trade Name	Formula	Reference(s)
aluminum powder	Al	24
aluminum chloride	Al_2Cl_6	14, 30, 35, 53, 82
alumina, aluminum oxide	Al_2O_3	10, 28, 35, 83
aluminum hydroxide oxide	$AlOOH$	10
cryolite	K_3AlF_6	10, 14, 82
potassium dawsonite	$KAl(OH)_2CO_3$	10
sodium dawsonite	$NaAl(OH)_2CO_3$	10
aluminum hydroxide	$Al(OH)_3$	10
aluminum ion	Al^{3+}	38, 84
alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	14, 82
acetylacetonatoaluminum	$Al(C_5H_7O_2)_3$	43
aluminum sulfate	$Al_2(SO_4)_3$	35
arsenic trichloride	$AsCl_3$	12
barium oxide	BaO	28
barium nitrate	$Ba(NO_3)_2$	35, 44, 84
barium hydroxide	$Ba(OH)_2$	14, 82
barium chloride	$BaCl_2$	14, 82
bismuthoxycarbonate	$Bi_2O_2CO_3$	24
calcium acetate	$Ca(C_2H_3O_2)_2$	49
calcium chloride	$CaCl_2$	24, 44, 49, 84
calcium carbonate	$CaCO_3$	28, 49, 50
calcium hydroxide	$Ca(OH)_2$	50
calcium fluoride	CaF_2	50
gypsum, calcium sulfate	$CaSO_4 \cdot \frac{1}{2}H_2O$	6, 49
calcium tartarate	$CaC_4H_4O_6 \cdot 4H_2O$	49
aqueous cerium	Ce^{3+}	84
ammonium cerium nitrate	$(NH_4)_2Ce(NO_3)_6$	24

SURVEY OF METAL COMPOUNDS TESTED FOR FIRE SUPPRESSION ACTIVITY (CONTINUED).

Common and/or Trade Name	Formula	Reference(s)
aqueous cobalt	Co^{2+}	38, 84
acetylacetonatocobalt(III)	$Co(C_5H_7O_2)_3$	26, 43
cyclopentadienylcobalt dicarbonyl	$Co(CO)_2C_5H_5$	46
aqueous chromium	Cr^{3+}	84
chromic oxide	Cr_2O_3	32, 85
chromium oxychloride	CrO_2Cl_2	8 ,12, 16, 57, 86, 87
acetylacetonatochromium(III)	$Cr(C_5H_7O_2)_3$	43
chromiumhexacarbonyl	$Cr(CO)_6$	21, 23, 32, 58
chromic acid	CrO_3	32
potassium chromate	K_2CrO_4	35
cesium carbonate	Cs_2CO_3	24
aqueous copper	Cu^{2+}	38, 84
cuprous chloride	$CuCl$	30, 31, 50
cupric chloride	$CuCl_2$	24, 35
cupirc oxide	CuO	35
basic copper carbonate, malachite	$CuCO_3 \cdot Cu(OH)_2$	24
iron powder	Fe	24
aqueous iron	Fe^{3+}	38, 84
iron pentacarbonyl	$Fe(CO)_5$	8, 12, 16, 21, 30, 31, 43, 47, 48, 54, 57, 60, 86, 87, 88
acetylacetonatoiron(III)	$Fe(C_5H_7O_2)_3$	43
potassium ferrocyanide	$K_4Fe(CN)_6$	26
potassium ferrocyanide trihydrate	$K_4Fe(CN)_6 \cdot 3H_2O$	11, 26
	$Na[Fe(CN)_5NO] \cdot 2H_2O$	26
iron(II) carbonate	$FeCO_3$	24
iron(III) nitrate	$Fe(NO)_3$	62
acetylacetonatoiron(III)	$Fe(C_5H_7O_2)_3$	18
trifluoroacetylacetonatoiron(III)	$Fe(C_5H_4F_3O_2)_3$	18

SURVEY OF METAL COMPOUNDS TESTED FOR FIRE SUPPRESSION ACTIVITY (CONTINUED).

Common and/or Trade Name	Formula	Reference(s)
hexafluoroacetylacetonatoiron(III)	$Fe(C_5HF_6O_2)_3$	18
aqueous gallium	Ga^{3+}	84
germanium chloride	$GeCl_4$	12, 16
aqueous indium	In^{3+}	84
potassium vapor	K	8, 40
potassium sulfate	K_2SO_4	10, 11, 24, 26, 30, 35, 50
potassium carbonate	K_2CO_3	10, 11, 24, 28
potassium bicarbonate, Purple-K	$KHCO_3$	6, 10, 11, 24, 26,28, 29, 30, 31, 50, 52, 56, 89
potassium iodide	KI	10, 24,28, 35, 89
potassium bromide	KBr	24,28, 35
potassium chloride, Super-K	KCl	10, 11, 24,28, 29, 35
potassium fluoride	KF	24
potassium bicarbonate-urea, Monnex	$KHCO_3 \cdot NH_2C(O)NH_2$	10, 11, 29
potassium oxalate	$K_2C_2O_4$	8, 26, 28
potassium oxalate hydrate	$K_2C_2O_4 \cdot H_2O$	11, 26, 89
potassium dipivaloylmethane	$[(CH_3)_3CCO]_2CHK$	25
potassium perchlorate	$KClO_4$	24
potassium nitrate	KNO_3	24, 35
potassium hydrogen tartarate	$KHC_4H_4O_6$	24, 28
potassium tartarate	$K_2C_4H_4O_6$	28
potassium sodium tartarate	$KNaC_4H_4O_6 \cdot 4H_2O$	28
potassium dichromate	$K_2Cr_2O_7$	24
aqueous lanthanum	La^{3+}	84
aqueous lithium	Li^+	84
acetylacetonatolithium	$LiC_5H_7O_2$	43, 90
lithium acetate	$LiC_2H_3O_2$	43
lithium chloride	LiCl	24, 43

SURVEY OF METAL COMPOUNDS TESTED FOR FIRE SUPPRESSION ACTIVITY (CONTINUED).

Common and/or Trade Name	Formula	Reference(s)
lithium fluoride	LiF	24
lithium carbonate	Li_2CO_3	24, 28
magnesium vapor	Mg	34
aqueous magnesium	Mg^{2+}	84
talc	$Mg_3Si_4O_{10}(OH)_2$	6, 50
magnesium chloride	$MgCl_2$	43
magnesium carbonate	$MgCO_3$	6, 35
magnesium oxide, magnesia	MgO	28
manganese(II) chloride	$MnCl_2$	38, 39, 84
acetylacetonato-manganese(III)	$Mn(C_5H_7O_2)_3$	43, 91
manganese carbonyl	$Mn_2(CO)_{10}$	21
molybdenum disulfide	MoS_2	24
sodium vapor	Na	8, 40, 49
sodium chloride, BCD-Orange	$NaCl$	10, 11, 24, 30, 31, 49, 50, 52
sodium carbonate	Na_2CO_3	6, 11, 24,28, 30, 31, 35, 49, 50
sodium bicarbonate	$NaHCO_3$	6, 11, 13, 24, 26, 27, 28, 29, 30, 31, 50, 52, 83, 89
sodium iodide	NaI	10
sodium fluoride	NaF	50
sodium oxalate	$Na_2C_2O_4$	11, 26, 28, 49
sodium tetraborate, borax	$Na_2B_4O_7 \cdot 10H_2O$	6, 11
aqueous sodium	Na^+	38, 84
sodium sulfate	Na_2SO_4	24, 49
sodium sulfite	Na_2SO_3	49
sodium hydroxide	$NaOH$	30, 43, 49
acetylacetonatosodium	$NaC_5H_7O_2$	30, 43, 90
sodium tartarate dihydrate	$Na_2C_4H_4O_6 \cdot 2H_2O$	13, 28
sodium hydrogen tartarate	$NaHC_4H_4O_6$	28

88

SURVEY OF METAL COMPOUNDS TESTED FOR FIRE SUPPRESSION ACTIVITY (CONTINUED).

Common and/or Trade Name	Formula	Reference(s)
sodium bromide	$NaBr$	50
sodium nitrate	$NaNO_3$	35
sodium dipivaloylmethane	$[(CH_3)_3CCO]_2CHNa$	37
aqueous nickel	Ni^{2+}	38, 84
nickel chloride	$NiCl_2$	43
nickel tetracarbonyl	$Ni(CO)_4$	21
nickel carbonate	$NiCO_3$	24
aqueous lead	Pb^{2+}	38, 84
lead(II) oxide, litharge	PbO	14, 24, 35, 82
lead carbonate	$PbCO_3$	24
lead acetate	$Pb(C_2H_3O_2)_4$	30, 31, 43
tetraethyl lead	$Pb(C_2H_5)_4$	8, 12, 16, 22, 23, 42, 54
tetramethyl lead	$Pb(CH_3)_4$	54
acetylacetonatolead(IV)	$Pb(C_5H_7O_2)_4$	43
aqueous rubidium	Rb^+	43
rubidium carbonate	Rb_2CO_3	24
antimony trichloride	$SbCl_3$	8, 12
antimony pentachloride	$SbCl_5$	8, 54
tin(IV) oxide	SnO_2	10
tin(IV) iodide	SnI_4	10
ammonium chlorostannate	$(NH_4)_2SnCl_6$	45, 84, 92
tin(II) chloride dihydrate	$SnCl_2 \cdot 2H_2O$	24
tin(IV) chloride	$SnCl_4$	8, 12, 16, 54, 57
tetramethyltin	$Sn(CH_3)_4$	57, 93
aqueous strontium	Sr^{2+}	44, 84
strontium carbonate	$SrCO_3$	24
dimethyltellurium	$Te(CH_3)_2$	8, 23
titanium tetrachloride	$TiCl_4$	8, 12, 16, 54, 57

SURVEY OF METAL COMPOUNDS TESTED FOR FIRE SUPPRESSION ACTIVITY (CONCLUDED).

Common and/or Trade Name	Formula	Reference(s)
aqueous thallium	Tl^+	38, 84
uranium(IV) oxide	UO_2	33, 59, 94
uranyl nitrate	$UO_2(NO_3)_2$	33, 59, 84
ammonium vanadate	NH_4VO_3	84
sodium tungstate	Na_2WO_4	10
tungsten fluoride	WF_6	57
aqueous zinc	Zn^{2+}	84
zinc carbonate	$ZnCO_3$	24
portland cement	——	6
fire clay	——	6

APPENDIX B

CHEMICAL ABSTRACT REVIEW OF THE RUSSIAN LITERATURE

(This list complements the information provided in Table 3.)

1. Baratov, A. N., and Vogman, L. P., "Review of the Use of Powders for Suppressing Combustion and the Mechanism of their Fire-extinguishing Action," Materialy Soveshchaniya po Mekhanizmu Ingibirovaniya Tsepnykh Gazovykh Reaktsii, 1st 1970, 182-204. [CA, 80, 85359y; English abstract; Russian paper on hand.] Salts studied: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, RbBr, RbI. Data presented on 11 commercial powders.

2. Baratov, A. N., "Heterogeneous Inhibition of Flame and Powdered Substances for Extinguishing Fires," Zhurnal Vsesoyuznogo Khimicheskogo Obshchestv im. D. I. Mendeleeva, 1974, 19(5), 531-5. [CA, 82, 45980d; English title only; Russian paper on hand.] 14 commercial agents are listed.

3. Baratov, A. N., Vogman, L. P., Kobzar, V. N., Azatyan, V. V., Museridze, M. D., Dzotsenidze, Z. G., Petviashvili, D. I., and Namoradze, M. A., "Inhibition of Methane Flame by Salt Suspensions," Fizika Goreniya i Vzryva, 1976, (1), 72-5. [CA, 85, 7937z; English abstract; Russian paper on hand.] Methane-oxygen mixtures were studied, and a correlation was found between extinguishing efficiency and the rate constants for disappearance of H and O atoms on the surface of the particles. Salts studied: $K_2C_2O_4 \times H_2O$, $K_2Cr_2O_7$, K_2SO_4, KCl, K_2CO_3, $KHCO_3$, NaCl, Na_2CO_3, Na_2SO_4, NaF, $NaHCO_3$, $Na_2C_2O_4$, $NH_4H_2PO_4$, $(NH_4)_2C_2O_4 \times H_2O$.

4. Baratov, A. N., Vogman, L. P., Kobzar, V. N., Azatyan, V. V., Museridze, M. D., Dzotsenidze, Z. G., and Petviashvili, D. I., "Inhibition of a Methane Flame by Salt Aerosols," V sb., Goryuchest' Veshchestv i Khim. Sredstva Pozharotusheniya, 1974, (2), 4-21. [CA, 86, 92684c; English title only.] See previous entry, and note similarity of authors and subject.

5. Baratov, A. N., "Fire-extinguishing Agents," Itogi Nauki Tekh.: Pozharnaya Okhr. 1977, 2, 5-39. [CA, 87, 103946; English abstract.] Review; water, foams, powders, inert diluents, and halogenated compounds.

6. Kobzar, V. N., Baratov, A. N., Vogman, L. P., Azatyan, V. V., Dzotsenidze, Z. G., and Museridze, M. D., "Relation Between Fire-extinguishing Effectiveness of Salt Suspensions and the Recombination of Atoms on their Surfaces," Problemy Goreniya i Tusheniya Pozharov, Materialy Vseoyuznoi. Nauchno-Prakticheskoi Konferrrentsii, 4th 1975, 34-5. [CA, 88, 9193q; English abstract.] Salts studied: K_2SO_4, Na_2SO_4, $MgSO_4$, $NaHCO_3$, $(NH_4)_2C_2O_4$, Rb_2SO_4. gOCS measures the destruction of O atoms during the inhibition process and is a quantitative indicator of the inhibition effectiveness. Here, C is the effective extinguishing concentration and S is the specific surface area of the powder.

7. Ksandopulo, G. I., Novikova, S. P., and Piskunov, V. G., "Comparative Effectiveness of Powdered Inhibitors for Acetylene-air Flames Problemy Goreniya i Tusheniya Pozharov, Materialy Vseoyuznoi. Nauchno-Prakticheskoi Konferrrentsii, 4th 1975, 41-2. [CA, 88, 25106u; English abstract.] 16 powders studied; alkali metal halides, sulfates, carbonates, and organic acid salts. Particle size: 5-160 microns. 5-10 percent talc or potassium stearate added for friability. Most effective: KI, KBr, $(NH_4)_3PO_4$, and mixtures with $(NH_4)_2HPO_4$.

8. Azatyan, V. V., Baratov, A. N., Vogman, L. P., Dzotsenidze, Z. G., and Museridze, M. D., "Study of the Mechanism of the Extinguishing Action of Aerosuspensions of Salts," Khimicheskaya Fizika Protessov Goreniya i Vzryva. Kinetika Khimicheskikh Reactii 1977, 110-13. [CA, 88, 173094d; English title only; Russian paper in hand.] Salts: NaCl, KCl, Na_2SO_4, K_2SO_4. Gives coefficients for removal of H and O atoms.

9. Abuladze, M. K., Namoradze, M. A., Dzotsenidze, Z. G., Museridze, M. D., and Baratov, A. N., "Study of the Kinetics of the Heterogeneous Recombination of Hydrogen Atoms on the Surfaces of Chlorides of Alkaline Earth Metals," Soobshcheniya Akademii Nauk Gruzinskoi SSR, 1978, 90(2), 373-5. [CA, 89, 136359u; English abstract.]

10. Bezarashvili, G. S., Baratov, A. N., Azatyan, V. V., Museridze, M. D., Dzotsenidze, Z. G., and Kobzar, V. N., "Inhibition of Methane Flame by Powders of Inorganic Salts. I. Potassium Sulfate," Kinetika I Kataliz 1979, 20(3), 584-8. [CA, 91, 107518; English translation in hand.] When the expected temperature of the particles in the flame was estimated, it was found that for particles larger than 5 microns, the expected temperature was insufficient to cause melting or appreciable vaporization of the particles. It follows that one would anticipate heterogeneous, rather than homogeneous, processes to dominate extinguishment. It was found experimentally that the critical density of powder required to prevent propagation of the flame through the premixed gases was a linear function of the particle diameter. This finding was consistent with heterogeneous recombination of the "active centers" under kinetic (rather than diffusion) control.

11. Bezarashvili, G. S., Baratov, A. N., Azatyan, V. V., Museridze, M. D., Dzotsenidze, Z. G., and Kobzar, V. N., "Inhibition of Methane Flame by Powders of Inorganic Salts. II. Sodium Carbonate," Kinetika I Kataliz 1979, 20(3), 589-92. [CA, 91, 90922h; English abstract.] Inhibition of HCHO formation from $\times CH_3$ and O_2 was especially important. As in the case of K_2SO_4, heterogeneous processes on the surface of the particle dominate. The powder concentration required to prevent propagation of the flame front is about 10 percent of the weight of the methane-air mixture, and is essentially the same as that for K_2SO_4.

12. Bezarashvili, G. S., Baratov, A. N., Museridze, M. D., and Dzotsenidze, Z. G., "Effect of Sodium Sulfate Powders on the Limits of Methane Ignition," Soobshcheniya Akademii Nauk Gruzinskoi SSR, 1979, 94(1), 89-92. [CA, 91, 159862h; English abstract; Russian paper in hand.] The results here are very similar to those for K_2SO_4. About 10 wt% Na_2SO_4 is required, and the effectiveness increases with decreased particle size.

13. Abuladze, M.K., Namoradze, M. A., Dzotsenidze, A. G., Museridze, M. D., and Baratov, A. N., "Studies of Heterogeneous Recombination of Hydrogen and Oxygen Atoms on Alkali Metal Chloride Surfaces," Izvestiya Akademii Nauk Gruzinskoi SSR, Seriya Khimicheskaya, 1979, 5(3), 238-46. [CA, 92, 136067h; English abstract.] Rate constants are obtained for recombination of H and O on LiCl, NaCl, KCl, RbCl, and CsCl surfaces. Activation energy and preexponential coefficients are determined for the H + O reaction on LiCl, NaCl and KCl.

14. Azatyan, V. V., and Semenov, N. N., "Nonlinear Chain Termination in Branched Chain Processes," Problemy Khimicheskoi Kinetiki, 1979, 5-12. [CA, 93, 32292h; Russian paper in hand.]

15. Abuladze, M. K., Namoradze, M. A., Dzotsenidze, Z. G., Museridze, M. D., and Baratov, A. N., "Study of the Kinetics of Heterogeneous Recombination of Hydrogen and Oxygen Atoms on the Surface of Some Inorganic Salts," Goryuchest Veschestv i Khim. Sredstva Pozharotusheniya, (Moskva), 1979, (6), 156-60. [CA, 93, 97893z; English title only.]

16. Azatyan, V. V., Kislyuk, M. U., Tret'yakov, I. I., and Shavard, A. A., "Role of Chemisorption of Atomic Hydrogen During Chain Combustion of Hydrogen," Kinetika I Kataliz 1980, 21(3) 583-7. [CA, 93, 102032z; English abstract; Russian paper in hand.] Chemisorption of H on surfaces of reaction vessels (MgO, quartz, and W) results in heterogeneous chain termination and recombina-tion of H atoms. Chemisorbed atomic H reacts partially with gas-phase O.

17. Baratov, A. N., Gabrielyan, S. G., Petrova, L. D., and Kondenko, E. E., "New Combined Combustion Inhibitors," Goryuchest Veshchestv i Khim. Sredstva Pozharotusheniya. (Moskva), 1979, (6), 135-8. [CA, 93, 152491u; English title only.]

18. Azatyan, V. V., "Instability of the Surface State and Its Role in Chain Combustion," Kinetika Khimicheskikh Reaktsii, Materialy Vsesoyuznogo Simpoziuma po Goreniyu I Vzryvu, 6th, Alma-Ata, Sept 23-26, 1980, 53-6. [CA, 95, 64586q; English abstract; Russian paper in hand.] Study of free radical reactions in quartz vessels pretreated with HF. Surface becomes passivated and free radical losses decrease.

19. Baratov, A. N., and Myshak, Yu. A., "New Fire-extinguishing Agents in the Chemical Industry," Khimicheskaya Promyshlinnost. (Moskva), 1982, (10), 607-12. [CA, 98, 56576h; English title; Russian paper in hand.] Combinations of N_2, Halon-2402 and H_2O. Some data also on powders: K_2SO_4, Cs_2SO_4, Na_2SO_4, Li_2SO_4, Pb_2SO_4 [sic], KCl, NaCl.

20. Shebeko, Yu. N., Korol'chenko, A. Ya., and Baratov, A. N., "Mechanism of the Effect of Hydrogen Chloride and Hydrogen Bromide on Chemical Processes in the Combustion of Carbon Monoxide," Khimicheskaya Fizika, 1984, 3(1), 99-103. [CA, 100, 88185f; English abstract.]

    $H + HBr \circledR H_2 + Br$ contrasted with $H + HCl \circledR H_2 + Cl$. Inhibiting effect of HBr is much larger.

21. Shebeko, Yu. N., "Features of the Combustion of Rich Organic Mixtures with Air and the Upper Concentration Limits for Ignition," Zhurnal Fizicheskoi Khimii, 1984, 58(4), 866-70. [CA, 101, 9596k; English abstract.] Discusses a critical temperature (1000 - 1100 K), which correlates with the upper concentration limit for ignition.

22. Azatyan, V. V, "Chain Processes and Nonsteady-state Nature of Surface States," Uspekhi Khimii, 1985, 54(1), 33-60. [CA, 102, 120563g; English abstract; Russian paper in hand.] This review paper includes a discussion of heterogeneous termination of chain-branching reactions.

23. Azatyan, V. V., "Kinetic Aspects of Chemical Methods for Prevention and Extinguishing of Fires," Zhurnal Vsesoyuznogo Khimicheskogo Obshchestv im. D. I. Mendeleeva, 1985, 30(1), 4-12. [CA, 102, 151555k; Russian paper in hand.] Discusses Halon 2402. Some data on a mixture of PCl_3 with $C_2F_4Br_2$.

24. Baratov, A. N., "Use of Combustion Iinhibitors for Fire Extinguishing Zhurnal Vsesoyuznogo Khimicheskogo Obshchestv im. D. I. Mendeleeva, 1985, 30(1), 13-20. [CA, 102, 151556m; Russian paper in hand.] Primary emphasis on halon 2402. Some comparative data with Halon 1301 and other agents. Discussion of mechanism of inhibition.

25. Shebeko, Yu. N., and Korol'chenko, A. Ya., "Interrealtion Between the Normal Combustion Rate of Methane in Air and Nonequilibrium Concentration of Hydrogen Atoms in the Flame Front," Kinetika i Kataliz, 1986, 27(2), 270-4. [CA, 104, 227430e; English abstract.] Studies the kinetics of the high-temperature oxidation of CO to CO_2 in the presence of HBr inhibitor.

26. Bezarashvili, G. S., Lordkipanidze, D. N., Dzotsenidze, Z. G., Gordeziani, D. G., and Zizova, L. A., "Role of Chemical and Thermal Factors in the Heterogeneous Inhibition of Various Flames," Doklady Akademii Nauk SSSR, 1987, 293(4), 892-5. [CA, 107, 25630w; English translation in hand.] Calculations were used to test the hypothesis that heterogeneous chemical processes predominate in the inhibition of flames by particles. The hypothesis is verified for methane-air flames, but not for hydrogen-oxygen flames. In the latter, heat removal from the combustion zone explains the inhibition.

27. Shebeko, Yu. N., Korol'chenko, A. Ya., Baratov, A. N., Shamonin, V. G., "Effect of External Active-centers as Sources on Flame Propagation in a Methane-air Mixture," Zhurnal Fizicheskoi Khimii, 1990, 64(6), 1708-11. [CA, 113, 81405n; English abstract.] The primary effect of the external center is kinetic, not thermal.

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1. Brown, J. A., Jacobson, E., Dvorak, L. E., Gibson, J., Gupta, A., Metchis, K., Mossel, J. W., Simpson, T., Speitel, L. C., Tapscott, R. E., and Tetla, R. A., *Chemical Options to Halons for Aircraft Use*, DOT/FAA/CT-95/9, U.S. Department of Transportation, Federal Aviation Agency, Atlantic City New Jersey, February 1995.

2. Skaggs, S. R., and Tapscott, R. E., *Advanced Streaming Agent Program: Candidate Survey*, Final Report, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, December 1994. NMERI 1994/45

3. Tapscott, R. E., Moore, T. A., Kaizerman, J. A., Kibert, C. J., and Tetla, R. A., "Advanced Agent Halon Substitutes," *Proceedings, International CFC and Halon Alternatives Conference*, Washington, DC, pp. 644-648, 23-25 October 1995.

4. Tapscott, R. E., "Second-Generation Replacements for Halon," *Proceedings, First International Conference on Fire Suppression Research*, Stockholm and Borås, Sweden, pp. 327-335, 5-8 May 1992.

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